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Contents

Radov, A. P., Vainshtein, E. E., and Pavlenko, L. I. Tungsten and molybdenum in igneous rocks (as related to the geochemistry of tungsten)	497
ov, A. B. Organic carbon in sedimentary rocks (in relation to the presence of petroleum)	510
nan, M. D. Geochemical characteristics of weathering processes in nepheline syenites of Khibina Tundra	537
resenskaya, N. T., and Karpova, I. S. Thallium in ore minerals of the Verkhnyaya Kvaisha	552
n, B. I. Geochemistry of thallium in alkalic rocks, with Mt. Sandyk Massif (northern Kirgiziya) as an example	560
nov, E. I. Relationship between composition of rare earths and composition and structures of minerals	574
e, I. E., Starik, F. E., and Mikhailov, B. A. Shifts of isotopic ratios in natural materials	587
nov, V. I., Surkov, Yu. A., and Vilenskii, V. D. Isotopic shifts in natural uranium compounds	591
v, V. V. The fundamental stages of hydrothermal activity of Kamchatka and Kurile Islands volcanoes and the associated types of thermal waters	600
urg, A. I., Gorzhevskaya, S. A., Erofeeva, E. A., and Sidorenko, G. A. The chemical composition of isometric titanium-tantalum niobates.	615
din, L. S. The chemistry of aegirinization and nephelinization of pyroxene in the formation of metasomatic nepheline-pyroxene rocks (bijolites)	637
ussion: The number of factors of state in systems. D. S. Korzhinskii	641
article: The Seventh Session of the Committee on Determination of the Absolute Age of Geologic Formations. V. I. Baranov and K. G. Knorre	646
The Second All-Union Conference on Petrography. N. I. Khitarov	648

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TRANSLITERATION

There is no ideal system of translit-
erating Russian, each has its advantage
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used by *Chemical Abstracts*, partly be-
cause of its wide acceptance by other
journals and partly because of certain
advantages in alphabetization of names.
The principal differences between this
system and others in common use are as
follows:

Russian	Chem. Abs.	Other
X	kh	h
И	ts	tz
Щ	shch	sch
Ю	yu	iu
Я	ya	ia

TUNGSTEN AND MOLYBDENUM IN IGNEOUS ROCKS (AS RELATED TO THE GEOCHEMISTRY OF TUNGSTEN)

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Chemistry, Academy of Sciences, USSR, Moscow

Abstract

A systematic investigation of the W and Mo content in various rocks has been carried out with the aid of a spectrochemical graphic method of analysis worked by the authors. The average content in ultramafic rocks is: W 7.7×10^{-5} ; $2.3 \times 10^{-5}\%$; Mo/W = 0.3; in mafic rocks: W 8.5×10^{-5} ; Mo 2.2×10^{-4} ; in intermediate rocks: W 1.96×10^{-4} ; Mo $1.06 \times 10^{-4}\%$; Mo/W = 0.55, and in felsic rocks: W 1.43×10^{-4} and Mo $1.6 \times 10^{-4}\%$; Mo/W = 0.66. It has been shown that the average Mo and W contents in rocks increase parallel with the increase of SiO₂.

The geochemistry of tungsten is poorly known. It is thought of, as a rule, to be analogous to the geochemistry of molybdenum, which is somewhat better known. We know more of the behavior of tungsten in magmatic genesis than in differentiation of igneous rocks. Nevertheless, there are major differences in the geochemical behavior of tungsten and molybdenum, despite similarities in the behavior of their compounds in ore-forming processes. We may be reminded, for example, that the higher oxides of tungsten are more stable in hydrothermal and post-magmatic processes than the corresponding oxides of molybdenum. The sulfide of molybdenum is stable in comparable environments. These differences appear to be due to the different thermodynamic characteristics of these two elements, particularly to differences in the energy of formation of their oxides and sulfides. These energies in kilocalories are as follows:

MoS₂ — 54.19

MoO₃ — 157.6

WS₂ — 46.15

WO₃ — 171.4 [1a]

Data on the abundance of Mo and W in meteorites are very scarce. According to Brown [1], the known Mo and W content of the iron phase of meteorites ($1.66 \times 10^{-3}\%$ and $8.1 \times 10^{-4}\%$ respectively) is higher than the amounts in the silicate phase by 1 to 1.5 orders of magnitude. Molybdenum is more siderophilic or chalcophilic than tungsten. As regards the amounts and distribution of molybdenum in different igneous rocks and minerals, an appreciable amount of data has now accumulated, sufficient to give us a fairly complete view of the geochemistry of

molybdenum. Earlier investigators were apparently exaggerating the molybdenum content of igneous rocks. After studies by Sandell [2], Kuroda and Sandell [3], and many others in recent years, we are justified in assuming that we have an accurate idea about the geochemistry of molybdenum and there is no need here to review the literature already cited by A. P. Vinogradov [4], and Kuroda and Sandell [3]. So much more reason for us to direct our attention to the geochemistry of tungsten.

There are isolated determinations of tungsten in igneous rocks by Hevesy and Hobbie [5], Noddack and Noddack [6] and, later, by Sandell [2] or [16]. The relatively high content of tungsten in igneous rocks, of the order of $10^{-3}\%$ reported by Hevesy and Hobbie and Noddack and Noddack, was not confirmed by later investigations as we shall presently see. For the time being the results of Sandell and his co-workers may be accepted instead.

The tungsten content of igneous rocks (all granites), according to different authorities, is as follows:

Hevesy and Hobbie, 1933 [5]: $8 \times 10^{-3}\%$; Landergrén 1948 [7]: $7 \times 10^{-4}\%$

Noddack and Noddack 1930 [6]: $1.8 \times 10^{-3}\%$; Sandell 1946 [2]: $1.6 \times 10^{-3}\%$

However, Sandell's results apply only to 11 samples of felsic rocks, chiefly granites. Let us remember that already Hevesy and Hobbie, Noddack and Noddack, and others, had noted that, as a rule, tungsten exceeds molybdenum in igneous rocks. Sandell also observed that both molybdenum and tungsten increase in igneous rocks parallel with the increase of SiO_2 . The scarcity of data on tungsten in rocks is due to the difficulty of its determination at concentrations of 10^{-4} to $10^{-5}\%$.

DETERMINATION OF TUNGSTEN AND MOLYBDENUM IN ROCKS

Sensitivity of the spectrographic determination of tungsten is relatively low. It never exceeds $5 \times 10^{-4}\%$ [8] and is much lower, in most instances, about 10^{-2} to $10^{-3}\%$ [9, 10, 11, 12]. The limit of spectrographic detection of molybdenum is somewhat greater than ca. $10^{-4}\%$. Direct utilization of the spectrographic method in the determination of molybdenum and tungsten in magmatic rocks is possible, therefore, only after a preliminary enrichment of these metals in the test materials. Following the enrichment procedure, Scobie [13] and Wilson and Fieldes [14] were able to increase the sensitivity of the spectrochemical determinations of tungsten in rocks and soils to about $2 \times 10^{-5}\%$ and $7 \times 10^{-5}\%$ respectively. In rock samples, tungsten was quantitatively determined spectrographically in the sediment, after absorption of tungsten by aluminum hydroxide from dilute solution. In the case of soils, spectrographic analysis was applied to the sediment obtained after preliminary enrichment of the sample by decomposition with hydrofluoric acid and the subsequent collection of tungsten by cinchonine ($\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$) from the solution. Some photocolorimetric procedures

the determination of tungsten in rocks are also known [15, 16], and the sensitivity of about $5 \times 10^{-5}\%$ tungsten. We determined tungsten and molybdenum spectrographically after their preliminary enrichment in the test materials. Aliquots of rock samples (± 1 g) were fused with soda. Then these melts were treated with water (ca. 150 mls.); next the sediments were filtered and washed with 1% aqueous soda. The filtrates, containing tungsten and molybdenum, were acidified with hydrochloric acid, to about 0.18 to 0.2 normality (with respect to either HCl or HNO_3), so as to inhibit the gelation of the $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ gel. The filtrates were treated then with tannin and with methyl violet by which tungsten and molybdenum were precipitated. The precipitate was filtered off, dried, ignited, weighed, and divided into two portions in which molybdenum and tungsten were determined spectrographically [17].

Radioactive isotopes were used in ascertaining the optimum conditions for the analysis. It has been established [18] that such well known reagents as nitron, methylene blue, phenyl hydrazine, gelatine, etc., do not collect tungsten or molybdenum by co-precipitation, even when the concentration of tungsten is as $1:2 \times 10^5$ (i.e. 5 ppm W or 5 mg W per liter). On the other hand, the tannin-methyl violet mixture is able to co-precipitate the metals of interest at dilutions up to about 5×10^{-10} grams per liter (i.e. 0.1 micrograms W per liter). At a tungsten concentration of the order of magnitude of $4 \times 10^{-5}\%$, the enrichment procedure employed by us was sufficient for all practical purposes to assure its quantitative precipitation as proved by control determinations. Neither heating of the test solution on a steam bath nor its prolonged aging had any effect on the quantitative collection of tungsten by the tannin-methyl violet mixture. There was a slight decrease in the co-precipitation of tungsten only when the tannin:methyl violet ratio was considerably in excess of 2:1.

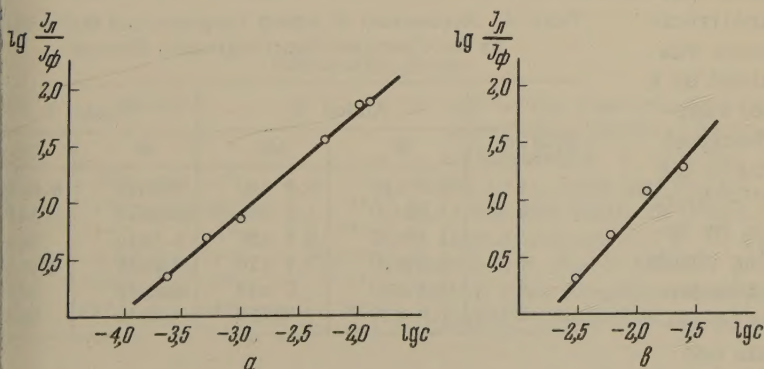


Fig. 1. Nomograms for spectrographic determination of Mo(a) and W(b) in rocks.

Molybdenum was determined spectrographically, in the ashed concentrate, by the Qu-24 quartz spectrograph with the 3-lens condenser and the DC arc, as follows:

The electrodes were carbon, with cavities 2.5 mm deep and 3.5 mm in diameter; the spectrograph slit was 0.02 mm. Ten mg sample aliquots were run at 10 a with an arcing interval of 2.5 minutes. The aliquot was a mixture of the sediment obtained by the chemical enrichment of the rock (about 2 mg) with a silicate base (about 18 mg) free from any detectable admixtures of tungsten and molybdenum by preliminary tests. The spectra were recorded on the Type II "spectrographic" films with the sensitivity of 8 or 11 units on the GOST Scale. The standards employed in construction of the nomograms were prepared from the same base which was used to dilute the samples before the analysis. The analytical line for Mo was 3170.35 Å.

Tungsten was determined in the sediments by the optical glass spectrograph ISP-51A with dispersion in the 4300 Å ~ 3 Å/mm field. Under such conditions, line 4294.6 Å may be used in the determination of tungsten because it is not overlapped by lines of other elements present in the rocks. A DC arc was the excitation source. Time required for volatilization of the sample and all other conditions of the analysis were the same as in the determination of molybdenum. The spectra were recorded on Type II "spectrographic" films, with a sensitivity of 22 units on the GOST Scale. The nomograms for the determinations of tungsten and molybdenum were constructed by the "three-standard" method, with the Log R and Log C coordinates. The nomograms are linear for the concentration fields of interest (Fig. 1). Sensitivity of the spectrochemical method for molybdenum and tungsten, as here described, is $2 \times 10^{-6}\%$ and $5 \times 10^{-5}\%$ respectively. The spectrographic results are reproducible within $\pm 7.8\%$ for Mo and $\pm 10\%$ for W.

Absence of any systematic errors

in the analytical procedures was ascertained by a series of especially designed problems of the "added"-"found" type (i.e. by determining yields of added known amounts of molybdenum and tungsten) as well as by comparisons

Table 1. Recoveries of Added Tungsten and Molybdenum by the Chemical-Spectrographic Method

Expt. No.	Added %		Found %	
	W	Mo	W	Mo
1	9.8×10^{-5}	6.4×10^{-4}	9.7×10^{-5}	6.5×10^{-4}
2	1.23×10^{-4}	1.9×10^{-4}	1.3×10^{-4}	2.1×10^{-4}
3	1.48×10^{-4}	5.5×10^{-5}	1.4×10^{-4}	5×10^{-5}
4	1.73×10^{-4}	2.4×10^{-4}	1.5×10^{-4}	2.6×10^{-5}
5	2.1×10^{-4}	5×10^{-4}	2.2×10^{-4}	4×10^{-4}
6	5.5×10^{-4}	1.05×10^{-4}	4.5×10^{-4}	9×10^{-5}

of the results on molybdenum obtained by (1) direct spectrographic analysis, (2) chemical-spectrographic analysis, and (3) the polaro-

mic methods [19]. The results of these comparisons were entirely satisfactory. Some of them are reported as examples in Figures 1 and 2.

Table 2. Comparison Between Determinations of Molybdenum in Granites by Spectrographic and Polarographic Analysis

Rock Sample	% Molybdenum	
	Spectrographic	Polarographic
T-1	2.3×10^{-3}	2.7×10^{-3}
T-2	6.3×10^{-4}	7.3×10^{-4}
T-3	1.6×10^{-2}	1.8×10^{-2}
T-4	3.4×10^{-4}	3.1×10^{-3}
T-5	2.3×10^{-4}	2.8×10^{-4}
T-6	2×10^{-4}	2.5×10^{-4}
T-7	2.2×10^{-4}	2.5×10^{-4}
T-8	1×10^{-4}	0.95×10^{-4}

MATERIALS

The problem in the present study was to obtain data on the tungsten content of principal types of igneous rocks, to determine the W ratio in these rocks and the average content of tungsten in the Earth's crust, in order to undertake later studies of the processes by which tungsten accumulates. Different types of igneous rocks were selected for the analysis.

Ultramafic rocks are represented, first of all, by dunites from different areas in Ural and in the north of the Siberian Platform. For the purpose of comparison, we include also some serpentinites from Ural.

Ultramafic Rocks

9)	Dunite	N. of Siberian Platform, Gulin Intrusion, Sadyba (NIIGA, Leningrad; collected by E. M. Epstein)
3)	Dunite	Arctic Ural, Syum Keu Massif
0)	Meimechite*	N. of Siberian Platform (NIIGA, Leningrad; collected by E. M. Epstein)
(49)	Dunite	Arctic Ural, Rai-Iz Massif
3)	Dunite	Central Ural, Konzhakovskii Kamen (IGEM; collected by O. A. Vorobeva)

Meimechi River. An ultramafic magmatic rock consisting of phenocrysts of olivine, pseudomorphs of pale yellow serpentine after olivine, and dark opaque matrix with small amygdaloids filled by serpentine or carbonate. First observed and described in the north of the Siberian Platform.

6 (865/51)	Dunite	Arctic Ural, Syum-Keu Massif
7 (133/49)	Dunite	Arctic Ural, Rai-Iz
8 (884/51)	Dunite	Arctic Ural, Syum-Keu Massif
9 (1008)	Peridotite	N. of Siberian Platform, Gulin Intrusion, (NIIGA, Leningrad; collected by E. M. Epstein)
10 (2001)	Pyroxenite	Aldan, Konder Massif (VAGT; Aldan Vilyui Expedition; collected by V. M. Moralev)
11 (215)	Serpentinite M-9	Collected by Z. V. Studenikova
12 (348)	Serpentinite M-10	Collected by Z. V. Studenikova
13 —	Dunite mixture (1020, 1021, 1022, 1023, 1025, 1026)	Saba - Voikor Massif, Arctic Ural (IGEM; collected by Markovkina)
14 (572)	Serpentinite M-65	Collected by Z. V. Studenikova

Mafic rocks are represented by basalts and diabases from Kamchatka, Caucasus, and Baikal Region, as well as by a series of gabbros from different areas in the Union.

Mafic Rocks

1 (1034)	Basalt	Kamchatka, Kirgurich Volcano, Klyuchevskaya Sopka (collected by S. I. Naboko)
2 (1040)	Basalt	Kamchatka, Tolbachino Volcano; collected by S. I. Naboko)
3 (1039)	Basalt	Klyuchevskaya Sopka, Bilyukai Crater (collected by S. I. Naboko)
4 (M-84)	Diabase	Caucasus (collected by Z. V. Studenikova)
5 (M-83)	Diabase	Caucasus (collected by Z. V. Studenikova)
6 (812)	Diabase	Metamorphosed Archean, Baikal (collected by D. S. Korzhinskii)
7 (No. 5)	Diabase	A young medium-grained diabase dike, Mys(Cape) Berezovyi, Archean (collected by D. S. Korzhinskii)
8 (1028)	Gabbro-Diabase	At a tributary of Olenek River, E. Siberia (collected by A. P. Lebedeva, IGEM)
9 (1035)	Gabbro-Diabase	Picritic, Norilsk (collected by N. I. Golevskii)
10 (B-47)	Gabbro	N. Osetiya, headwaters of Tsei River (collected by Z. V. Studenikova)
11 (1030)	Gabbro-Diabase	Vilyui River Basin (collected by A. P. Lebedeva, IGEM)

Intermediate rocks, granodiorites and diorites, were taken chiefly from a Caucasian Massif already described in detail.

Intermediate Rocks

-51)	Diorite	N. Caucasus, Mt. Yatyrgvarta (collected by Z. V. Studenikova)
+46)	Diorite	N. Osetiya, headwaters of Tsei River (collected by Z. V. Studenikova)
/T)	Diorite	N. Kirgiziya (collected by L. V. Tauson)
-15-2)	Granodiorite	N. Osetiya, headwaters of Aigamuga-Don River (collected by Z. V. Studenikova)
-50)	Granodiorite	NW Caucasus, Ashista River (collected by Z. V. Studenikova)
-32)	Granodiorite	N. Osetiya (collected by Z. V. Studenikova)
	Granodiorite	N. Kirgiziya (collected by L. V. Tauson)
-24)	Granodiorite	N. Caucasus, left bank of Laba River, Mt. Yatyrgvarta (collected by Z. V. Studenikova)

Felsic rocks--granites--were taken from Caucasus, Kazakhstan, Lake Baikal territories. Most of our samples had already been mined for rare and dispersed chemical elements.

Felsic Rocks

)	Massive biotite granite	A ₂ (Precambrian, Kotov Formation), Baikal (collected by D. S. Korzhinskii)
)	Bi - "Atv." porphyroid granite	A ₂ (Precambrian, Kotov Formation), Baikal (collected by D. S. Korzhinskii)
/53)	Granite	Kazakhstan (collected by Afanasev)
53)	Granite	Betpakdala, Kazakhstan (collected by Afanasev)
	El'dzhurtin granite	Caucasus, Tyrny-Auz (collected by Z. V. Studenikova)
)	El'dzhurtin granite	Caucasus, Tyrny-Auz (collected by Z. V. Studenikova)
	El'dzhurtin granite	Caucasus, Tyrny-Auz (collected by Z. V. Studenikova)
	El'dzhurtin granite	Caucasus, Tyrny-Auz (collected by Z. V. Studenikova)

EXPERIMENTAL RESULTS AND DISCUSSION

Granitic rocks are especially difficult in the analysis for tungsten and molybdenum, inasmuch as they contain less tungsten and molybdenum than the other igneous rocks. Our results are reported in Table 3. As one may see, there is not much variation in tungsten: $7.7 \times 10^{-5}\%$ to $2.5 \times 10^{-4}\%$, with the average of $7.7 \times 10^{-5}\%$ and the average W of 0.3. There is definitely more tungsten than molybde-

Table 3. Tungsten and Molybdenum in Ultramafic Rocks

Sample	%Mo	%W	Mo/W
1. Dunite (1009); N. of Siberian Platform	3.2×10^{-5}	$< 6 \times 10^{-5}$	0.53
2. Dunite (1006); Arctic Ural	5×10^{-6}	7.4×10^{-5}	0.07
3. Meimechite (1010); Siberian Platform	2×10^{-5}	2.5×10^{-4}	0.08
4. Dunite (126/49); Arctic Ural	1.1×10^{-5}	7×10^{-5}	0.15
5. Dunite (1003); Central Ural	1.2×10^{-5}	5×10^{-5}	0.24
6. Dunite (865/51); Arctic Ural	7×10^{-5}	$< 6 \times 10^{-5}$	1.1
7. Dunite (133/49); Arctic Ural	1.5×10^{-5}	$< 6 \times 10^{-5}$	0.25
8. Dunite (884/51); Arctic Ural	9.5×10^{-6}	$< 6 \times 10^{-5}$	0.17
9. Peridotite (1008)	3.7×10^{-5}	3.5×10^{-5}	1.0
10. Pyroxenite (2001)	$< 5 \times 10^{-6}$	$< 6 \times 10^{-5}$	0.08
11. Serpentinite, (215) M-9	3.5×10^{-5}	$< 6 \times 10^{-5}$	0.58
12. Serpentinite, (348) M-10	9×10^{-6}	6.5×10^{-5}	0.14
13. Dunite mixture, 1020-1026	1.4×10^{-5}	3.3×10^{-5}	0.42
14. Serpentinite (572) M-65	1.3×10^{-5}	4.4×10^{-5}	0.30
Average	2.3×10^{-5}	7.7×10^{-5}	0.3

num in ultramafic rocks. There is no conspicuous difference between the amounts of tungsten and molybdenum in pyroxenites, dunites, peridotites, and serpentinites. Our molybdenum average for ultramafic rocks is very close to the average reported by Kuroda and Sandell [3] (Table 4). Our results for molybdenum confirm the distinction between the silicate phase of meteorites and ultramafic (terrestrial) rocks which was noted previously by Vinogradov [22]. The distinction lies in the fact that several rare and dispersed elements are present in much higher concentrations in stony meteorites (chondrites) than in ultramafic rocks (higher by 0.5 to 1 order of magnitude). Even their absolute amounts are very small both in the silicate phase of meteorites and in ultramafic rocks. This holds for U, Rb, Sn, Ti, and several others, including Mo, inasmuch as the silicate phase is reported to contain $6 \times 10^{-5}\%$ Mo, as against $4 \times 10^{-5}\%$ Mo in ultramafic rocks [Kuroda and Sandell, 3]; our figure for ultramafic rocks is $2.3 \times 10^{-5}\%$ Mo. The tungsten content of mafic rocks (Table 5), basalts and gabbros, is only a little higher than it is in ultramafic rocks. One may notice a tendency toward higher tungsten in basalts and diabbases ($1 \times 10^{-4}\%$) than in gabbros (about $6 \times 10^{-5}\%$).

There is about twice as much molybdenum in the mafic rocks we examined than in comparable rocks examined by Ishimori [20] and Sandell (Table 4). Other investigators, however, report $2 \times 10^{-4}\%$ Mo in such materials. As the result, the Mo/W ratio increases to over on the average. If validity of our generalization were to be sustained by further empirical data, this would mean that molybdenum is predominant over tungsten in basic rocks. Before considering this conclusion, however, we must obtain more data.

Table 4. Molybdenum Content of Rocks According to Different Authors

Rock	Sandell 1943	Pavlenko 1954	Ishimori 1951	Kuroda & Sandell 1954	Onishi & Sandell 1955	Present Report
	Per cent molybdenum					
Silicate phase of dieterorites				6×10^{-5} (3)		
Ultramafic				4×10^{-5} (23)		2.2×10^{-5} (14)
Mafic	2×10^{-4} (7)*		9×10^{-5} (10)	9×10^{-5} (59)	2×10^{-4} (6)	2.2×10^{-4} (11)
Intermediate			1×10^{-4} (15)	7×10^{-5} (29)		1×10^{-4} (8)
Felsic	2.5×10^{-4} (13)	2×10^{-4} (24)	3×10^{-4} (10)	1.1×10^{-4} (35)		1.6×10^{-4} (8)

*Figures in parentheses refer to number of analyses.

Molybdenum shows the same tendency as tungsten. Its average is lower, on the whole, in basalts and diabases than in gabbros ($1.1 \times 10^{-4}\%$ as against $1.9 \times 10^{-4}\%$ respectively.) Whereas the data on molybdenum and tungsten in ultramafic and mafic rocks are somewhat scattered, they are relatively uniform. For intermediate and felsic rocks (Tables 6 and 7) tungsten fluctuates between $1.4 \times 10^{-4}\%$ and $3.3 \times 10^{-4}\%$ in diorites and granodiorites with an average of $1.9 \times 10^{-4}\%$; tungsten is higher in granites, on the whole, with an average of $2.4 \times 10^{-4}\%$ but the limits of its variation are only $2 \times 10^{-4}\%$ to $3.3 \times 10^{-4}\%$. The molybdenum content is just as stable. Our molybdenum average for granites coincides very well with results by other investigators (Table 4) and especially with our earlier results [4]. There is almost twice as much tungsten as molybdenum in intermediate rocks. Among igneous rocks, granites are richest in tungsten, with a Mo/W of 0.7.

Table 5. Tungsten and Molybdenum Content of Mafic Rocks

Rock and Source	% Mo	% W	Mo/W
1. Basalt (1034); Kamchatka	9.5×10^{-5}	$< 6 \times 10^{-5}$	1.6
2. Basalt (1040); Kamchatka	4.4×10^{-4}	1.6×10^{-4}	2.7
3. Basalt (1039); Kamchatka	3.1×10^{-4}	1.1×10^{-4}	2.8
4. Diabase (M-84); Caucasus	1.2×10^{-4}	7×10^{-5}	1.8
5. Diabase (M-83); Caucasus	4.2×10^{-4}	1.4×10^{-4}	3.0
6. Diabase (812); Baikal	1.9×10^{-4}	7.3×10^{-5}	2.7
7. Diabase (No. 5); Baikal	9.4×10^{-5}	6×10^{-5}	1.6
8. Gabbro-diabase (1028); E. Siberia	7.8×10^{-5}	5×10^{-5}	1.6
9. Gabbro-diabase (1035); Norilsk	3.5×10^{-4}	8×10^{-5}	4.4
10. Gabbro B-47; N. Osetiya	1.7×10^{-4}	6×10^{-5}	2.8
11. Gabbro-diabase (1030); E. Siberia	1.5×10^{-4}	5×10^{-5}	3.0
Average	2.2×10^{-4}	8.5×10^{-5}	2.5

Table 6. Tungsten and Molybdenum Content of Intermediate Rocks

Rock and Source	% Mo	% W	Mo/W
1. Diorite (B-51); N. Caucasus	9.5×10^{-5}	1.5×10^{-4}	0.6
2. Diorite (B-46); N. Osetiya	1.3×10^{-4}	2×10^{-4}	0.6
3. Diorite (98/1); N. Kirgiziya	9×10^{-5}	1.4×10^{-4}	0.6
4. Granodiorite (B-15-2); N. Osetiya	6.6×10^{-5}	2.1×10^{-4}	0.3
5. Granodiorite (M-50); NW. Caucasus	1.2×10^{-4}		
6. Granodiorite (M-32); N. Osetiya	1×10^{-4}	3.3×10^{-4}	0.3
7. Granodiorite (1); N. Kirgiziya, Kazakhstan	1.5×10^{-4}	2.6×10^{-4}	0.6
8. Granodiorite (M-24); N. Caucasus	9.2×10^{-5}		
Average	1.1×10^{-4}	1.99×10^{-4}	0.55

Our data are very close to Sandell's earlier results on tungsten in 11 samples of granites. His results show that tungsten fluctuates between $1.1 \times 10^{-4}\%$ and $2.6 \times 10^{-4}\%$ with an average of $1.6 \times 10^{-4}\%$ and a Mo/W ratio of 0.96.

Syenite (from Northern Caucasus, from the upper basin of Malaya Laba River) examined in the present study contains $4.6 \times 10^{-5}\%$ Mo and $6.3 \times 10^{-5}\%$ W; Mo/W = 0.69.

It follows from the foregoing data that both tungsten and molybdenum increase gradually in ultramafic to felsic rocks, parallel to increases in SiO_2 . This trend is such that the Mo/W also increases from 0.3 in ultramafic rocks to 0.7 in granites (Table 8 and Fig. 2).

A few words now about molybdenum and tungsten in sedimentary rocks. A mixed composite sample representing 7614 samples of clays of different age, from the Russian Platform, and a mixed composite of 6107 samples of sands* were examined for tungsten and molybdenum.

The content of molybdenum and tungsten in the clay composite was found to be $7.4 \times 10^{-5}\%$ and

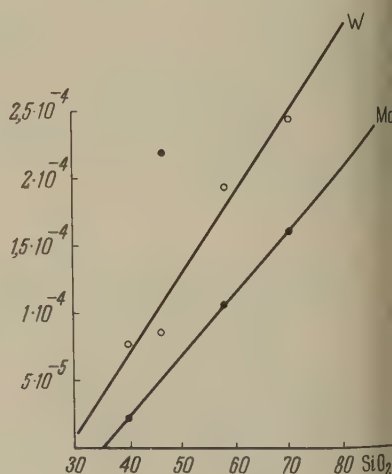


Fig. 2. Variations in tungsten and molybdenum contents of igneous rocks relative to their SiO_2 content.

*These samples of clays and sands were placed at our disposal by A. B. Ronov who prepared them from the average samples representative of different facies and climatic environments of the sedimentation.

Table 7. Tungsten and Molybdenum Content of Felsic Rocks

Rock and Source	% Mo	% W	Mo/W
1. Massive biotite granite (38a); Baikal	1.4×10^{-4}	2×10^{-4}	0.7
2. Granite (70c); Baikal	9.5×10^{-5}	1.9×10^{-4}	0.5
3. Granite (42); Kazakhstan	2.2×10^{-4}	1.9×10^{-4}	1.0
4. Granite (84/53); Kazakhstan	1.8×10^{-4}	2.6×10^{-4}	0.7
5. Eldzurtin granite (01); Caucasus	1.3×10^{-4}	2.3×10^{-4}	0.6
6. Eldzurtin granite (058); Caucasus	1.1×10^{-4}	2.6×10^{-4}	0.4
7. Eldzurtin granite (04); Caucasus	2.1×10^{-4}	3.3×10^{-4}	0.6
8. Eldzurtin granite (062); Caucasus	2.3×10^{-4}	2.8×10^{-4}	0.8
Average	1.6×10^{-4}	2.4×10^{-4}	0.7

$10^{-4}\%$ respectively, with the corresponding Mo/W ratio of 0.40, much like in igneous rocks. The sand composite showed $4 \times 10^{-5}\%$ and $1.6 \times 10^{-4}\%$ W; Mo/W = 0.25. These results indicate a greater mobility of molybdenum than of tungsten in the weathering of igneous rocks. This may be a possible explanation of the fairly common enrichment of marine shales by molybdenum (and uranium) but not by tungsten.

CONCLUSIONS

We have demonstrated that the tungsten content increases in mafic to felsic rocks (from $7.7 \times 10^{-5}\%$ to $2.4 \times 10^{-4}\%$ respectively), parallel with the increase of the molybdenum content (from $2.3 \times 10^{-5}\%$ to $6 \times 10^{-4}\%$ respectively). Thus the content of both of these elements in igneous rocks increases parallel with increase of SiO_2 content. Tungsten exceeds molybdenum 1.5 to 2 times, on the average. Igneous rocks appear to be an exception. This generalization requires

Table 8. Average Content of Tungsten and Molybdenum in Rocks of Different Type (per cent)

	Ultramafic	Mafic	Intermediate
average	2.3×10^{-5}	2.2×10^{-4}	1.1×10^{-4}
range	$(< 5 \times 10^{-6} \text{ to } 7 \times 10^{-5})$	$(7.8 \times 10^{-5} \text{ to } 4.4 \times 10^{-4})$	$(9 \times 10^{-5} \text{ to } 1.5 \times 10^{-4})$
average	7.7×10^{-5}	8.5×10^{-5}	1.9×10^{-4}
range	$(3.3 \times 10^{-5} \text{ to } 2.5 \times 10^{-4})$	$(7.3 \times 10^{-5} \text{ to } 1.6 \times 10^{-4})$	$(1.4 \times 10^{-4} \text{ to } 3.3 \times 10^{-4})$
W	0.29	2.5	0.56
Felsic			
average	1.6×10^{-4}		
range	$(9.5 \times 10^{-5} \text{ to } 2.3 \times 10^{-4})$		
average	2.4×10^{-4}		
range	$(1.9 \times 10^{-4} \text{ to } 3.3 \times 10^{-4})$		
W	0.7		

ould be $< 6 \times 10^{-5}$

further studies, however. There is a greater scattering of the tungsten data in the case of ultramafic and mafic rocks than in the case of intermediate and felsic rocks. Our results for molybdenum in different types of igneous rocks are in a good agreement with the results obtained by earlier investigators.

2. The average tungsten content of the earth's crust should be taken at $2 \times 10^{-4}\%$; the average molybdenum content at $1.5 \times 10^{-4}\%$, with an average Mo/W ratio close to 0.7.

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ORGANIC CARBON IN SEDIMENTARY ROCKS (IN RELATION TO THE PRESENCE OF PETROLEUM)

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Abstract

The author has studied the distribution of organic carbon (C_{org}) in 26,000 samples of rocks of different lithological composition and of different age and genesis, representing various facies and tectonic zones of the Russian platform both in oil basins and in provinces devoid of oil. Statistical treatment of these data has shown that in the distribution of C_{org} , according to the stratigraphic scale, an alternation of epochs of intensive and of insignificant accumulation of organic matter can be observed (Table 1, Fig. 1). All the deposits of caustobioherites (coals, petroliferous shales and oils) are closely tied to stratigraphic intervals with an increased content of scattered C_{org} . Comparison of data on the Russian platform with those of P. D. Trask and H. W. Patnode for the USA [31] establishes a similar character of alternation of periods of enrichment and impoverishment of scattered C_{org} in sedimentary strata (Table 2, Fig. 2). The average C_{org} content in rocks of oil basins is three times as high as in rocks of areas not bearing oil (Table 3, Fig. 3). In the oil basins the maximum C_{org} content is observed in sediments of marine nearshore deposits, representing epineritic environments; the minimum content—in sediments of continental and lagoonal environments and intermediate values—in sediments of open sea facies, representing infraneric and bathyal environments (Fig. 4). Among the marine epineritic sediments of oil basins (1.77%) and of provinces not bearing oil (0.32%) clays are richest in C_{org} (Fig. 5). The C_{org} distribution in various rock types of continental and lagoonal facies and of open sea facies is shown in Figs. 6 and 7 (Table 3). With the aid of quantitative litho-geochemical maps the C_{org} distribution in clayey (Fig. 8), carbonate (Fig. 9) and sandy (Fig. 10) upper Devonian beds of the Frasnian stage of the Russian platform has shown that in approaching the Volga-Ural oil basin the C_{org} content of the rocks increases, reaching its maximum value within the boundaries of the basin. This is seen most distinctly on the map for clay beds. A comparison with the map showing the change in the $\frac{Fe_2O_3}{FeO}$ ratio in clays of the same age (Fig. 11) shows parallel with the increase of C_{org} a successive increase in reducing conditions is observed, which becomes predominant in rocks of the oil basins. This indicates that the heightened C_{org} content created a regionally stable reducing medium in clayey sediments. On the one hand this has determined the transformation trend of the bitumen part of organic matter into oil, and on the other hand the changes of valence of iron in the clays.

1. INTRODUCTION

Thirty years ago, A. D. Arkhangel'skii [1] showed in his studies that there exists a definite relationship between the amounts of organic substance in clays and the oil in the Tertiary sediments of Northern Caucasus. Somewhat later, P. D. Trask and H. W. Patnode [31] carried out a study, immense in bulk, which included for the first time data on distribution and abundance of organic carbon in sedimentary rocks in practically every one of the post-Proterozoic geologic systems (except the Triassic). They performed 7052 determinations of C_{org} in samples of rocks representing different petroleum provinces of the United States of America. Unfortunately, these authors employed only a crude classification of their samples into "clastic" rocks (2245 analyses) and limestone (461 analyses) and even neglected to state what kinds of rocks were represented by the remaining 4346 analyses. Trask and Patnode generalized their findings in idealized small-scale maps showing regional variations of the $\%C_{org}$, the C/N ratio, etc., for different parts of the United States. Their maps were on the modern geographic base, without any consideration of facies-geologic environments, and for that reason are of limited value. The investigations of Arkhangel'skii, Trask and Patnode constituted the basis of all subsequent studies of quantitative abundance and qualitative composition of the organic matter in sedimentary rocks and in source rocks of petroleum, in particular [1, 30, 31]. The more recent developments in the geochemistry of petroleum, however, have been following only the second of these two lines of inquiry, namely qualitative studies of elemental composition and of categories of organic substance buried in ancient and modern sediments. This path has led the science to discoveries of new facts that to some extent deepened our understanding of the environments favorable for the accumulation of organic matter and of factors responsible for its transformation into petroleum [3, 4, 5, 11, 18, 25, 26, 28, 33, 34, and others]. Developments of quantitative studies, as indicated by Arkhangel'skii, Trask, and Patnode, were confined to oblivion, for all practical purposes. There are still major "blanks" in our knowledge, even in reference to certain elementary and yet fundamental aspects of the problem, and, first of all, in regard to the relationships governing the relative abundance of disseminated organic carbon in sedimentary rocks of the larger basins of sedimentation. We ought not to maintain, of course, that petroleum geologists are unaware of the importance of quantity, that is, the extent of accumulation of organic matter in sediments [4, 5, 27], although there is a great difference between the simple appreciation of the role of quantity in the buried organic matter and the exact knowledge of the relationships determining its presence in sediments. The present study was conducted with that very objective in mind, as to ascertain, with the Russian Platform as the example, the

relationships involved in the distribution of organic carbon in sedimentary rocks of different composition, origin, and age, within the boundaries of known and proved petroliferous and non-petroliferous provinces. Our assumption was that the role of quantity, in discovering possibilities of new and potentially economic petroleum districts, may be defined on the basis of systematic and reasonably complete regional data obtained by means of a standardized quantitative procedure.

There are numerous data scattered in the literature of our country on the determinations of organic carbon in Paleozoic and still younger sedimentary rocks in different parts of the Russian Platform [3, 11, 12, 14, 16, 19, 20, 27, and others]. All of these findings, however, are either confined to some small area or to some small section of the stratigraphic column. With very few exceptions [3, 11, 27, etc.], the results in question are only approximate indications of the average content of C_{org} in rocks of this or that stratigraphic complex and some of them are merely single or occasional determinations. It was not possible for us therefore to make use of these earlier data. We had to rely on our own experimental data obtained at the Laboratory of Geochemistry of Sedimentary Rocks, the V. I. Vernadskii Memorial Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR. Because of the obvious time-consuming character of the project, we had to omit the examination of organic matter by categories and the determination of its elemental chemical composition. We hope to return to these topics in the future.

Our test materials were drill cores from orientation and exploratory boreholes and, for the northwestern parts of the Russian Platform, we also used rocks from natural outcrops kindly placed at our disposal by A. I. Vete, R. F. Gekker, and D. V. Obruchev. In assembling the drill-core materials, we received the invaluable aid of the staff of the All-Union Research Institute of Geologic Exploration for Petroleum (VNIGNI),^a the All-Union Petroleum Research Institute of Geologic Exploration (VNIGRI),^b the All-Union Petroleum Research Institute (VNII),^c the All-Union Institute of Geologic Research (VSEGEI),^d the Geologic Bureau of Central Regions, the Government Research Institute of Mineral and Chemical Raw Materials (GIGKhS),^e the Mining Institute, the Petroleum Institute of the Academy of Sciences of the USSR, the Kuibysheft,^f The Leningrad Geological

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^fRegional Petroleum Offices, Kuibyshev and Saratov respectively. VPS.

au, the Saratovneft,^f the Union Office of Geological Prospecting (PK),^g and others.

In looking for our rock materials, we endeavored to arrive at a reasonably uniform distribution of the sampling sites throughout the area. This was especially important for the Devonian sediments that were employed in the preparation of a series of maps (Figs. 8, 9, 10, 11). The area of our study was bound approximately by 51° and 60° N. and 24° and 56° E., for the Paleozoic, with the inclusion also of the Mesozoic and Tertiary regions, down to the approaches to the Northern Caucasus in the instance of the Mesozoic and the Tertiary sediments. All of the stratigraphic subdivisions of the sedimentary mantle of the Russian Platform were represented by rock samples (Table 1).

In the vast majority of cases, we were analyzing not individual samples but standard composites prepared from the drillcores, so as to represent the required parts of the stratigraphic column, by means of separate composites of clays, sands, and carbonate rocks. The procedure for the preparation of such composites was described in our earlier publications [21, 23]. It is essential to point out, in the present connection, that our composites were prepared by taking into account the quantitative proportions of thickness of the clayey interbeds in sands and in carbonate rocks and the sum-total of thickness of clayey "packets" (sandy or carbonate) in the given part of the stratigraphic column. By such means our samples were made to be representative.

In all-in-all, we examined 418 composites of clays (representing 418 samples), 402 composites of sands (representing 6184 samples), 285 composites of carbonates (representing 10341 samples). Thus our studies, as a whole, embraced 25742 samples of sedimentary rocks representing all of the geologic systems and divisions (locally, also the Quaternary), from the Sinian to the Quaternary (Table 1). We examined samples from petroliferous as well as from definitely non-petroliferous basins characteristic of the different tectonic zones of the Russian Platform and of its different facies and geochemical environments of sedimentation. The total content of organic carbon in the composites was determined by the Knop Method.

All analyses included replicate determinations, with the permissible discrepancy between the results not over 0.05% C_{org.}. Where the discrepancies were above this threshold, the analyses were repeated. Determinations of total silica and carbon were also performed on all composites examined at the Laboratory. Some of the results have already been published [8, 9, 10, 21, 24].

In order to solve our problem we had to develop a method of interactive analysis of the regional trends in the concentrations of the

Table 1. Average Content of Organic Carbon in Different Types of Sediments of the Russian Platform

	Clays			Sands			Carbonate Rocks	
	Number of composites ^a	Number of samples in composites	%C _{org.}	Number of composites	Number of samples in composites	%C _{org.}	Number of composites	Number of samples in composites
Sinian, Sh ₃	33	1211	0.33	31	125	0.08	3	106
Cambrian, Cm	21	680	0.25	22	394	0.15	no carbonate rocks	
Ordovician, O	7	167	1.55	14	214	0.16	8	473
Gotlandian, S	6	531	0.23	1	5	0.11	5	379
Silurian, O + S	13	698	0.94	15	219	0.17	13	852
Lower Paleozoic, P _{z1}	67	2589	0.42	68	1864	0.12	16	958
Middle Devonian, D ₂	82	1193	0.48	97	1287	0.15	48	783
Franiian, D ₁	101	2039	0.84	104	1393	0.19	84	2768
Famenian, D ₃	10	266	0.44	9	117	0.17	37	2213
Upper Devonian, D ₃	114 ^b	2340	0.78	113	1510	0.19	121	4981
Devonian, D	196	3533	0.66	210	2797	0.17	169	5764
Lower Carboniferous, C ₁	28	338	1.32	20	135	0.58	27	815
Middle Carboniferous, C ₂	23	261	0.43	15	103	0.29	23	92
Upper Carboniferous, C ₃	-	-	-	-	-	-	14	520
Carboniferous, C	51	599	0.92	35	238	0.45	64	2527
Lower Permian, P ₁	1	22	0.30	-	-	-	14	706
Ufa Tier, puf	7	91	0.24	7	102	0.50	-	66
Kanзан Tier, P ₂ ^{kaz}	9	170	0.61	5	72	0.36	-	-
Tatar Tier, P ₂ ^{tat}	10	404	0.09	9	429	0.15	-	-
Upper Permian, P ₂	27 ^c	695	0.30	21	603	0.31	4	66
Permian, P	28	717	0.30	21	603	0.31	18	772
Middle and Upper Paleozoic, P _{z 2 + 3}	275	4849	0.67	(266)	(3638)	(0.22)	(251)	(9063)
Paleozoic, Pz	342	7438	0.62	(334)	(5502)	(0.20)	(267)	(10021)
Triassic, T	6	127	0.05	5	76	0.12	-	-
Lower Jurassic, J ₁	3	17	0.93	3	21	0.40	-	-
Middle Jurassic, J ₂	4	60	0.99	7	41	0.48	-	-
Upper Jurassic, J ₃	9	185	0.91	12	62	0.59	6	19
Jurassic, J	19 ^d	336	1.05	24 ^e	179	0.60	8 ^f	44
Lower Cretaceous, Cr ₁	7	179	1.26	11	121	0.59	1	14
Upper Cretaceous, Cr ₂	4	72	0.54	10	85	0.24	6	161
Cretaceous, Cr	11	251	1.00	21	206	0.42	7	175
Mesozoic, Mz	36	714	0.87	50	461	0.48	15	219
Quaternary, Q	4	1023	1.05	20	141	0.40	2	191

organic carbon disseminated in the sediments against the background of the general lithologic-facies environments in the sedimentation basins. A quantitative lithologic-geochemical map is such a method [21, 22]. The base of this map was a lithologic-facies map of the territory here studied. As we know, a lithologic-facies map shows different facies-sedimentation environments, the lithologic zones, and indications of the ancient boundaries of the erosion by water. The stratigraphic aspects of our composite samples were determined by the stratigraphic principles underlying the lithologic-facies base. The results of the analyses for C_{org} were plotted as circles on the lithologic-facies base. Six standard sizes of the circles were employed representing proportionally the number of samples in the composites (Figs. 8, 9, 10, 11). We were enabled by such means to show on the map the number of composite samples representing different parts of the Platform. After plotting the circles on the base map we drew the following isograds of the C_{org} percentages: 0.25; 0.50; 0.75; 1.00; 2.50; 5.00. By means of these isograds, we defined the boundaries of areas within the Platform poor or rich in the disseminated organic carbon. Two series of the maps were so prepared. The first series consisted of three maps showing the distribution and abundance of organic carbon in clays, carbonates, and sands of the Franian Tier (Figs. 8, 9, and 10 respectively). The second series also consisted of three maps for the same kind of sediments in the Zhivetskii* Tier but we are not publishing them here, because

a In the original: "chislo srednikh prob", "number of average samples". It is evident, however, that composite samples are meant, both from the context and the usage of Vinogradov et al., e.g. in *Geokhimiya* No. 1, 1956. VPS

b This number includes one supplementary composite of 35 samples whose age was dated with reliability not exceeding D.*
 c This number includes one supplementary composite of 30 samples whose age was dated with reliability not exceeding P.†
 d This number includes three supplementary composites of 74 samples whose age was dated with reliability not exceeding J.‡
 e This number includes two supplementary composites of 55 samples whose age was dated with reliability not exceeding J.‡
 f This number includes two supplementary composites of 25 samples whose age was dated with reliability not exceeding J.‡

* Apparently as undifferentiated Upper Devonian. VPS

† Apparently as undifferentiated Middle Permian. VPS

‡ That is, undifferentiated Jurassic. VPS

*After Givais (?), Belgium; the uppermost tier of the Middle Devonian. "Tier", ("Yarus") consists of "suites" ("svity"), in the Russian Stratigraphy, the term meaning essentially the same as "series" in the U. S. usage. The Division, e.g. Lower, Middle, or Upper, consists of tiers (there seems to be no analogues of

we are not publishing them here, because of the limitations of space in the magazine article. Maps showing variations in the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio in clayey sediments of Franian and the Zhivetskii† Tiers were constructed by the analogous procedure.

2. STRATIGRAPHIC DISTRIBUTION OF ORGANIC CARBON IN SEDIMENTS OF DIFFERENT TYPES

The data on the average content of organic carbon in clays, sands, and carbonate rocks of different geologic age are summarized in Table 1. The totals in this table show that, among the three types of rocks here discussed, the clays are the richest ones in organic carbon, with the average of 0.67 for the 9217 samples. The C_{org} average for the sands is slightly over one-third of this value: 0.24% (the average of 6184 samples); the carbonates contain 0.23% (the average of 10341 samples). As to the Russian Platform average, for all types of sediments, it is 0.40% C_{org} , by the analysis of 1105 composites represented

Table 2. Average Content of Organic Carbon in Sedimentary Rocks of the Russian Platform and of the United States of America

System	Russian Platform			U.S.A.	
	No. of composites	No. of samples in composites	% C_{org}	No. of analyses	% C_{org}
Sinian (Sn_2)	68	2588	0.20	n.d.*	n.d.*
Cambrian and Ordovician (Cm + O)	72	1928	0.33	278	0.68
Gotlandian (S)	12	915	0.20	73	0.34
Devonian (D)	575	12094	0.37	338	0.58
Lower Carboniferous (C_1)	75	1288	0.69	296	0.85
Pennsylvanian (Middle and Upper Carboniferous, $\text{C}_2 + \text{C}_3$)	75	2076	0.25	881	0.76
Permian (P)	67	2092	0.26	118	0.30
Triassic (T)	11	203	0.08	n.d.	n.d.
Jurassic (J)	51	559	0.71	30	0.43
Cretaceous (Cr)	39	632	0.54	1419	0.86
Tertiary (Tr)	47	1265	0.87	3619	1.68
Quaternary (Q)	14	122	0.20	n.d.	n.d.
Average or sum	1105	25,742	0.40	7052	1.08

*n.d. = not determined

tiers in the U. S. Groupings). (In the English abstract prepared by the Russian author, the term is translated as "stage." E.W.H.) The Russian "series" ("serii") are the same as "suites", but the term is used only for metamorphic rocks. The Russian "complexes" ("komplekxy") are analogues of "series" and "suites" but the term is reserved only for volcanic or igneous rocks. VPS †Not published in the present article.

25,742 samples. This magnitude is only a little over one-third of average organic carbon in sedimentary rocks of the U. S. A. (Table which is 1.08% (average of 7052 samples), according to Trask and Patnode [31]. The difference between the Russian Platform and the U. S. A. is explained by the fact that Trask and Patnode were studying only the petroliferous provinces entirely, while our value represents both petroliferous and non-petroliferous districts, with a definite preponderance of the latter (Table 3). If, however, we compare the U. S. A. results only with the results for the petroliferous parts of the Russian Platform (the average of 4610 samples is 0.85% C_{org}), there is a little difference between the two, for all practical purposes. The C_{org} averages reported by V. A. Uspenskii and co-workers [32] are based on a small number of analyses of samples chiefly from petroliferous districts, hence their excessively high magnitudes. The average percentage of organic carbon increases upwards in the stratigraphic column as it fluctuates between enrichment and impoverishment of the sediments with respect to disseminated organic substance (Table 1). The directions of these fluctuations are the same for all types of rocks but amplitudes of the fluctuations are not the same. The greatest amplitudes are observed in clays, with clearly marked maxima and minima, as shown by the curves of the average content of organic carbon in sediments on the time scale (Fig. 1). These differences suggest periodic alternations of strong and weak accumulations of organic substance in sedimentary beds. The peaks of the accumulation belong to the middle epochs of the Caledonian, the Hartz, and the Alpine sedimentation cycles (O, C_1 , and J to Cr_1), while sediments at the beginnings and at the ends of these cycles contain appreciably lower amounts of organic substance (Cm, S, P, T, Q). This periodicity is complicated by the secondary maxima (D_3^1 , $P_2^{kaz.}$, Tr). It is with these particular stratigraphic spans, with their "highs" of disseminated organic carbon in the sediments, that all of the larger accumulations of caustobioliths of the Russian Platform are associated. In other words, every one of the maxima on the Clarke curves for the disseminated organic carbon has its counterpart in the synchronous accumulations of economically important organic carbon. The kind of a caustobiolithic deposit, i.e. whether it is coal, combustible shale, or oil, that is located in the Russian Platform, is determined, in every epoch, by the entire complex of definite tectonic, climatic, and geochemical environments of the accumulation and transformation of the original organic matter. The Ordovician maximum on the C_{org} distribution curves (Fig. 1) has its counterpart in the zone of the bituminous shale deposits in the southwest of the Platform. No oil deposits of this age could be discovered, so far, although their presence is entirely possible, in the

in the sense of "regional average" or "background". VPS

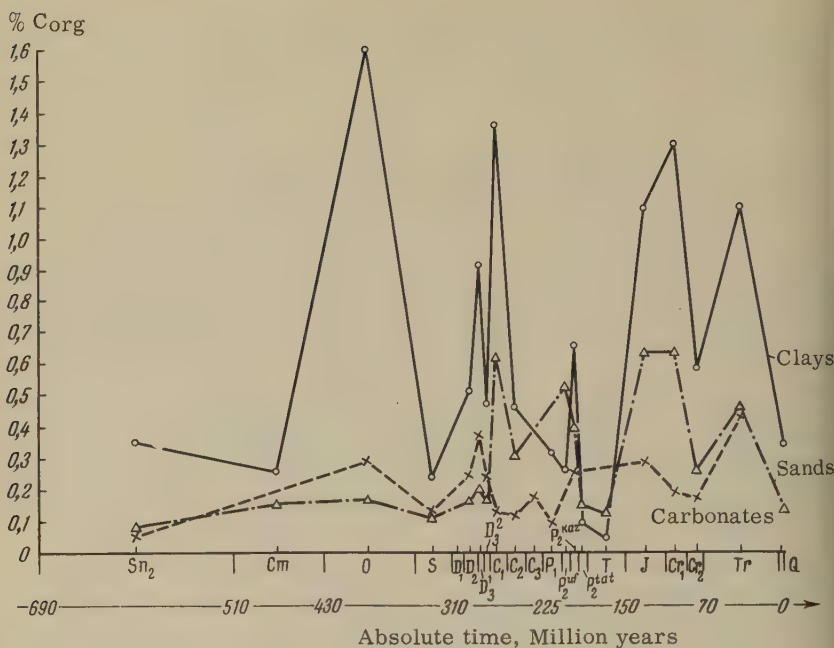


Fig. 1. Variations in the average content of organic carbon in clays, sands, and carbonate rocks of the Russian Platform. (Based on analyses of 418 composites (9217 samples) of clays, 402 composites (6184 samples) of sands, and 285 composites (10341 samples) of carbonate rocks.)

western parts of the Baltic territories or in the adjoining parts of Poland, in our opinion, under favorable structural and facies-lithologic conditions.* The *Franian* maximum has its counterpart in the largest deposits of oil in the Volga-Ural districts. The *Visaian* maximum left its imprint, in the west of the Platform, in the coal deposits of the Moscow Basin, and in the east—in the zone of coastal-marine sediments—in oil deposits of the Carboniferous suite of the Second Baku. The very small *Kazan* peak of the curves is represented by a small coal measure in the northeast of Tataria and by the expressions of oil in the Kinel Ridge (the Buguruslan oil fields). The *Jurassic* maximum is represented by the Emba Coal Measures and by the Povolzhe fuel shales. The *Lower Cretaceous* and the *Tertiary* maxima materialized in the southeast of the Platform, as the North-Caucasian and the Emba oil fields.

*The Ordovician maximum appears to be somewhat high, because its average %C_{org}. (in the Ordovician clays) was calculated from a relatively small number of the analyses of the available test rock materials (Table 1).

It was our interest to compare the results for the Russian Platform and for the U. S. A. For the sake of this comparison, we regulated our data to the same stratigraphic basis as was employed Trask and Patnode [31] in their breakdown of the analyses. In this case, too, we had to calculate the C_{org} averages for the sedimentary complexes as a whole (Table 2). We were enabled by these calculations to make the comparisons, on the basis of stratigraphically equivalent zones in the two areas, between the organic carbon content of the sedimentary complexes (entire systems) of the Russian Platform and of North America (Fig. 2). We were greatly impressed by analogies in the enrichment-impoverishment periodicity sequence, with respect to disseminated organic carbon, in these two territories, far away from one another,

on different continents and in different hemispheres. A coincidence of this sort can hardly be accidental. It suggests rather a historic tendency, common for the entire earth, a tendency toward periodic increases and reductions in the biotic intensity of organisms whose remains are found in the form of disseminated organic matter in sedimentary rocks. During periods of increased biotic activity of organisms, there is a consequent increase in the buried biotic mass, which, in the Ordovician, the Carboniferous, and the Tertiary, is followed by periods of a relative weakening of the activity of organisms and of the resulting appreciable reduction in the quantity of the buried biotic mass, were the Silurian and the Permian. The first one of

these maxima was contingent chiefly on marine flora and fauna, since terrestrial plants played a very modest role in the Ordovician, whereas the Carboniferous and the Tertiary maxima represent the combined biogenic activities of marine and terrestrial organisms. The alternations of minima and maxima in the development of organic life of the earth are closely related to changes in the tectonic and the physico-geographical environments. The periods of abundant



Fig. 2. Variations in the average content of organic carbon in sedimentary rocks of the Russian Platform and of the United States of America. (Based on analyses of 1024 composites (23052 samples) for the Russian Platform and of 7052 individual analyses reported by P. D. Trask and H. W. Patnode for the U.S.A.)

life correspond to the periods of a relative calm, tectonically; of the great marine transgressions; and of the preponderance of humid and, on the whole, temperate climates, while the minima coincide with regressions and with abrupt expansions of arid zones.

The extent of preservation of disseminated organic carbon in sedimentary rocks is a problem of considerable importance. The quantity of organic carbon decreases during diagenesis of the sediments and during the authigenic formation of minerals. N. M. Strakhov showed that the expenditures of C_{org} may be estimated approximately by the amounts of pyrite in sedimentary rocks.

As shown by the calculations, there is almost 10,000 times as much organic carbon in the disseminated state as there is in the petroleum reservoir rocks. On the basis of the earlier comparisons by V. A. Sokolov and V. E. Khain [26, 35], of the results of Trask and Patnode on the C_{org} in sedimentary rocks of different age with the distribution of coal reserves of the world (according to P. I. Stepanov) and of the oil reserves, by the geologic systems, we were enabled to state a hypothesis as to a relationship between these magnitudes. We may now state definitely that such a relationship indeed exists, as an expression of a direct dependence between the distribution of the clark abundances of organic carbon on the time scale and its economic accumulations.

The regular association of oil deposits with stratigraphic complexes regionally enriched in organic carbon indicates that the bulk of oil deposits is localized within the source-rock stratigraphic complexes, despite the definite importance of vertical migration of oil.

3. DISTRIBUTION OF ORGANIC CARBON IN DIFFERENT FACIES OF PETROLIFEROUS AND NON-PETROLIFEROUS ROCKS FROM DIFFERENT PROVINCES

The analytical data on C_{org} in representative composite samples of sediments in the Russian Platform were classified into groups by the following indications. First of all, the composites were divided into two inclusive categories: 1) Representatives of sediments from petroliferous provinces; 2) Representatives of territories known to be definitely non-petroliferous.

Composites within these two categories were classified further into three basic types, depending on the sedimentation environments by which their facies were determined, namely: a) continental and lagoonal; b) coastal-marine; c) sediments of open seas.

In referring our composites to this or that category and type, we were guided by the Atlas of Lithologic-Facies Maps of the Russian Platform prepared by the V. I. Vernadski Memorial Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR.

Facies	Regional character	Clays			Sands			Carbonate rocks			Average for all sedimentary rocks		
		No. of composites	No. of samples in composites	%C _{org.}	No. of composites	No. of samples in composites	%C _{org.}	No. of composites	No. of samples in composites	%C _{org.}	No. of composites	No. of samples in composites	%C _{org.}
Continental and lagoonal	Petroliferous	10	175	0.19	9	114	0.40	6	254	0.11	25	543	0.25
	Non-petroliferous	120	2233	0.36	143	1918	0.14	104	3600	0.15	367	7751	0.22
	Sum or average	130	2408	1.35	152	2032	0.15	110	3854	0.15	392	8294	0.22
Coastal-marine	Petroliferous	64	756	1.77	61	825	0.42	17	259	0.32	142	1840	1.02
	Non-petroliferous	139	3227	0.32	135	2316	0.21	39	126	0.17	313	6569	0.26
	Sum or average	203	3983	0.78	196	3141	0.28	56	1285	0.21	455	8409	0.49
Open-sea (pelagic)	Petroliferous	37	905	0.99	5	31	0.37	44	1291	0.57	86	2227	0.74
	Non-petroliferous	48	1921	0.85	49	980	0.33	75	3911	0.17	172	6812	0.41
	Sum or average	85	2826	0.91	54	1011	0.33	119	5202	0.32	258	9039	0.52
All types	Petroliferous	111	1836	1.37	75	970	0.41	67	1804	0.47	253	4610	0.85
	Non-petroliferous	307	7381	0.42	327	5214	0.20	218	3537	0.16	852	21,132	0.27
	Sum or average	418	9217	0.67	402	6184	0.24	285	10,341	0.23	1105	25,742	0.40

and by the All-Union Petroleum Institute of Research and Geologic Exploration [2], with suitable corrections, as indicated in the more recent publications [13, 14, 15, 17, 21, 29], and others. Wherever there was an overlapping of the facies, the classification of the sample was determined by the preponderances of facies of the given type.

The results of subsequent statistical recalculations are summarized in Table 3 and illustrated by a series of diagrams (Figs. 1 through 7). Figure 3 shows that there is three times as much disseminated carbon in sediments from the petroliferous territories as there is in sediments from the non-petroliferous ones. For example, clays from petroliferous provinces contain 1.37% C_{org.}, on the average, whereas there is only 0.42% C_{org.}, on the average, in clays from non-petroliferous provinces. The differences are about the same in the case of sands and of carbonate rocks, although their absolute content or organic carbon is appreciably lower (Table 3). These figures indicate an existence of a certain minimum of organic substance in the major sedimentary complexes below which the transformations of disseminated organic carbon cannot be conducive to the development of economic accumulations of petroleum as the result of qualitative alterations of the

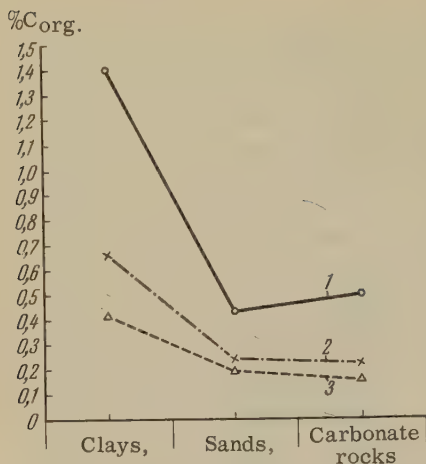


Fig. 3. Average content of organic carbon in different types of sedimentary rocks from petroliferous and non-petroliferous areas of the Russian Platform. (Based on analyses of 1105 composites (25742 samples); 1—petroliferous areas; 2—the Russian Platform as a whole; 3—non-petroliferous areas.)

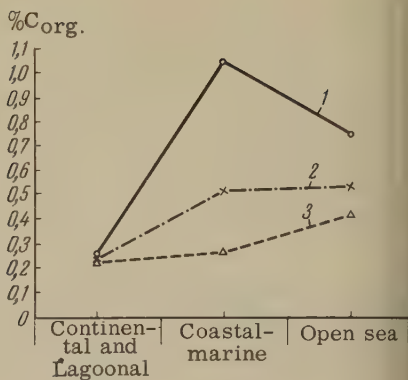


Fig. 4. Average content of organic carbon in sediments of different facies zones in petroliferous and non-petroliferous areas of the Russian Platform. (Based on analyses of 1105 composites (25742 samples); 1—petroliferous areas; 2—the Russian Platform as a whole; 3—non-petroliferous areas.)

bitumens. This critical level lies somewhere between the $\%C_{org.}$ averages for the petroliferous and the non-petroliferous areas, i. e. between 1.4 and 0.4%, and it is probably closer to the first one of these two figures.

Figure 4 illustrates the distribution of organic carbon between different facies of the sediments. Its curves represent this distribution separately for petroliferous and for non-petroliferous provinces. In petroliferous provinces, the highest content of $C_{org.}$ is found in the coastal-marine facies (1.02%) and the lowest one in the continental-lagoonal facies (0.25%); the intermediate averages (0.74%) belong to the open-sea facies. As to the rest—the non-petroliferous areas of the Russian Platform—the relationships are not quite the same: the highest content of organic carbon is found in the open-sea facies (0.41%) and the lowest one (0.22%) in the continental and lagoonal facies; the intermediate values (0.26%) are found in the coastal-marine facies and the lowest ones (0.22%) in the continental and lagoonal facies. The bulk of organic carbon, in the instance of petroliferous provinces, is concentrated therefore in the *coastal-marine facies*. It is these facies, “the clots of life”, in the words of V. I.

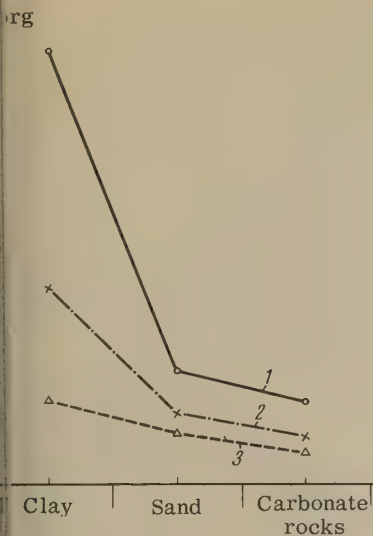


Fig. 5. Average content of organic carbon in different types of coastal-marine sediments in petroliferous and non-petroliferous areas of the Russian Platform. (Based on analyses of 455 composites (8409 samples); 1—petroliferous areas; 2—the Russian Platform as a whole; 3—non-petroliferous areas.)

Shadskii, that give origin to petroleum [6]. The distribution of organic carbon in coastal-marine facies is illustrated diagrammatically in Fig. 5. One may easily see that the greatest accumulations of organic carbon are found in clays: 1.77%

Fig., average, in petroliferous areas, as against a little less than one-fifth of this value (0.32%) in non-petroliferous areas. This difference between petroliferous and non-petroliferous areas, in the case of coastal-marine sediments of the other two types (i.e., sands and carbonate rocks), is substantially reduced because of their relatively low content of organic carbon. For example, the average Corg. of sands in petroliferous areas is 0.42, as against 0.21 of sands outside their boundaries—a mere two-fold difference. In the case of carbonate rocks, the corresponding averages are 0.32 as against 0.17% (Table 3).

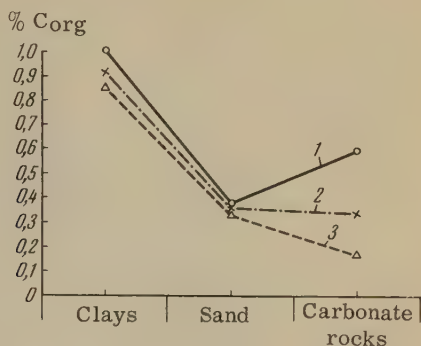


Fig. 6. Average content of organic carbon in different types of pelagic sediments in petroliferous and non-petroliferous areas of the Russian Platform. (Based on analyses of 258 composites (9039 samples); 1—petroliferous areas; 2—the Russian Platform as a whole; 3—non-petroliferous areas.)

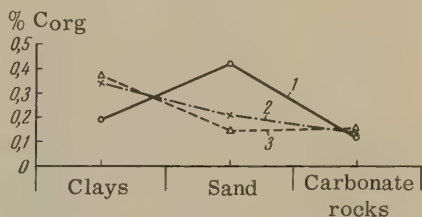


Fig. 7. Average content of organic carbon in different types of continental and lagoonal sediments in petroliferous and non-petroliferous areas of the Russian Platform. (Based on analyses of 392 composites (8294 samples); 1—petroliferous areas; 2—the Russian Platform as a whole; 3—non-petroliferous areas.)





Fig. 8. Lithologic-geochemical map showing distribution of disseminated organic carbon in clays of the Upper Devonian, the Franian Tier^a, of the Russian Platform. Clays and sands of the Lower Shchigry^b Horizon are practically ubiquitous and are omitted from the lithologic-facies base of the map.

Key: 1—areas of erosion by water; 2—sands with inter-layers of clays; 3—red sands and clays; 4—sands and clays; 5—sands and clays with inter-layers of limestones; 6—clays; 7—sands and clays with ‘packets’^c of carbonate rocks and gypsum; 8—carbonate rocks with ‘packets’^c of gypsum, sands, and clays; 9—carbonate rocks and gypsum with inter-layers of marls and clays; 10—carbonate rocks, gypsum, anhydrite, and rock salt; 11—carbonate rocks, gypsum, and anhydrite with inter-layers of marl; 12—limestones, marls, sands, and clays; 13—limestones, sands, and clays; 14—limestones with inter-layers of sands and clays; 15—composites of less than 10 samples; 16—composites of 10 to 20 samples; 17—composites of 20 to 30 samples; 18—composites of 30 to 40 samples; 19—composites of 40 to 50 samples; 20—composites of more than 50 samples; 21—boundaries of water-eroded areas; 22—% C_{org} isograds; (in Fig. 11—the Fe₂O₃/FeO ratio isograds); 23—isoegrads of the average % C_{org} in the profile; (in Fig. 11—isoegrads of the average Fe₂O₃/FeO ratio in the profile); 24—boundaries between lithologic-facies zones.

^aThe lowest Tier of the Upper Division of the Devonian System. VPS

^bAfter Shchigry (or Shchigrov); the lowermost horizons of the Upper Devonian, in the center of the Russian Platform, consisting of gray, green, brown, red, and mottled alternating marls, sandstones, and limestones. VPS

^c‘packet’ (‘paket’) means essentially ‘interbedded’, with the implication on relatively thin layers of sediments of different types, in irregular alternations. VPS

The relationships in the *open-sea facies* are not quite the same (Fig. 6). The organic carbon averages for petroliferous and non-petroliferous areas are about the same, for clays (0.99 and 0.85% respectively). The averages for sands, lower as they are, are also essentially the same (0.37 and 0.33% respectively) for both petroliferous and non-petroliferous areas. There are great differences, however, in the carbonate rocks. The $C_{org.}$ average (0.57%) for carbonate

rocks from petroliferous areas is higher than for the sandstones, whereas it is definitely lower than the sandstone average, in the case of carbonate rocks from non-petroliferous areas (0.17%).

There are anomalous relationships in the *continental-lagoonal facies* within petroliferous provinces (Fig. 7). Although the $\%C_{org.}$ is definitely lower in such facies, on the whole, than in the other facies of the same provinces, the $C_{org.}$ maxima (0.40%) are found in the sands and its minima in the clays and in the carbonate rocks (0.19 and 0.11% respectively). This leaves no doubt that the sands—good collectors—were enriched with the organic substance as the result of an upward migration of bitumens from the underlying petroliferous horizon. Outside the boundaries of petroliferous provinces, as a rule, we observe a progressive lowering of the $\%C_{org.}$ from clays to sands (0.36 to 0.14% respectively) and to carbonate rocks (0.15%).

The statistical analysis leads us to the following conclusions:

1. Sedimentary rocks in petroliferous provinces contain much more disseminated carbon than is found in sedimentary rocks of non-petroliferous provinces.
2. The greatest accumulations of $C_{org.}$ in petroliferous provinces are associated with coastal-marine facies of sediments.
3. The bulk of organic substance in near-shore sediments in petroliferous provinces is accumulated in the clays.
4. The hypothesis of inorganic origin of petroleum cannot account for the absence of economic accumulations in continental and lagoonal sediments—so abundant in the territories here studied and so exceedingly poor in disseminated organic substance.

4. ORGANIC CARBON AND GEOCHEMICAL ENVIRONMENT IN THE AREA OF THE BASIN OF SEDIMENTATION

In the foregoing discussion, we suggested certain statistical relationships in the distribution of organic carbon in different types of rocks, depending on their facies and oil-bearing characteristics. Like all abstractions of such kinds, statistical relationships indicate only some general tendencies involved in the problem, but, as such, do not and cannot reflect the details of the actual distribution of $C_{org.}$ in a sedimentation basin of the size of the Russian Platform. We at-

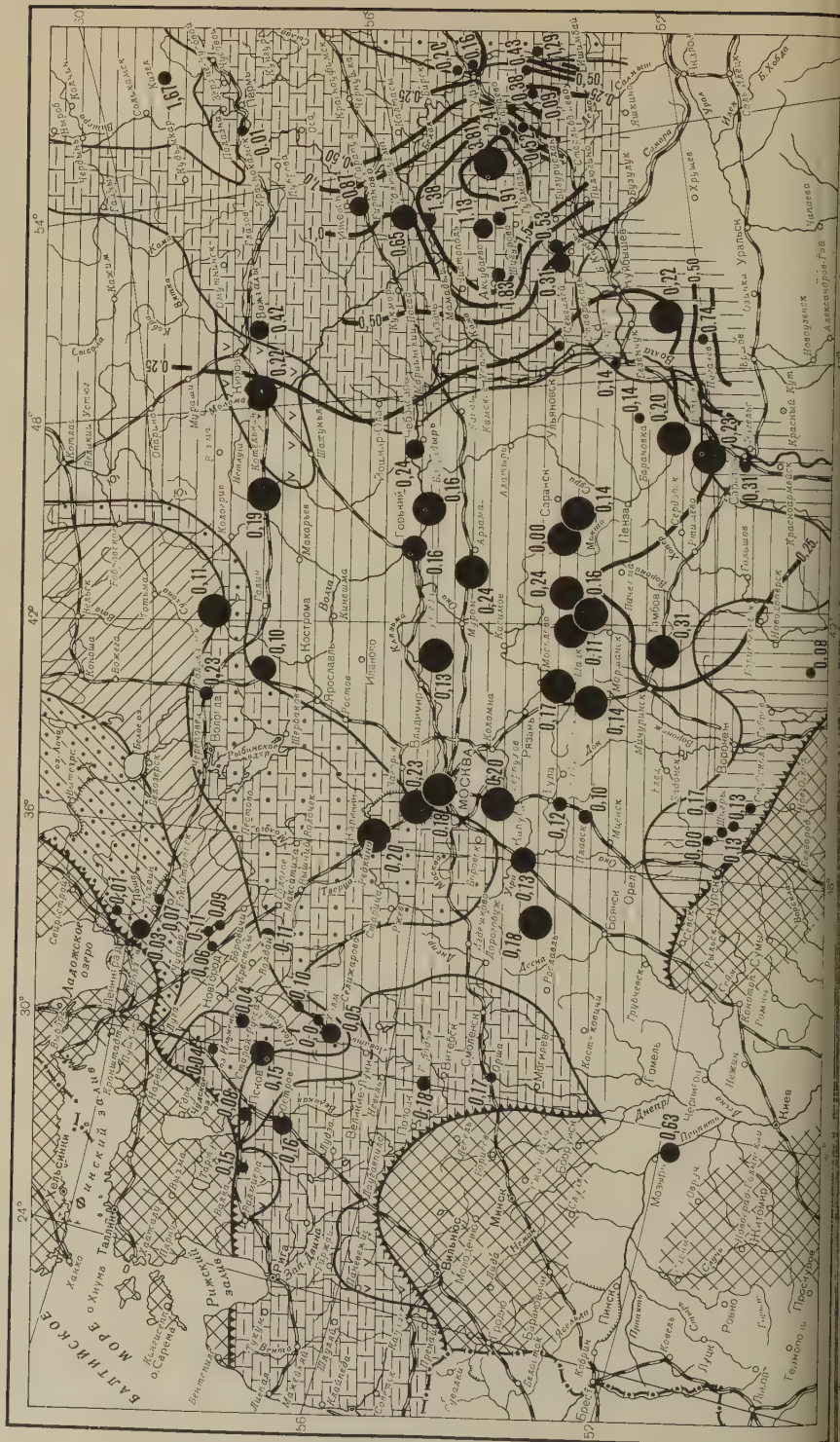
ted to find such detailed expressions by means of quantitative geologic-geochemical maps.

In the selection of materials for these studies, in harmony with the aim, it became necessary to assemble a stratigraphic complex which would be petroliferous in some parts of the basin and non-petroliferous in others, while embracing, at the same time, all of the rock facies and all of the facies-environments here investigated. These requirements were best satisfied by sediments of the Franian Tier.

As we know, this Tier contains some of the largest deposits of petroleum in the Volga-Ural Oil Region, in the eastern part of the Platform, whereas the same sediments are definitely non-petroliferous in the western part of the same Platform. Sedimentation environments of the Tier's facies are distinguished also by their variations. Continental-lagoonal sediments are preponderant in the northwest of the basin, with occasional wedges of coastal-marine or marine masses, while in the central parts of the Platform we find intricate intergradations of all of these facies of sedimentary rocks and a gradual passing out of continental and lagoonal rocks toward the east.

Finally, in the east of the Platform, in the Volga-Ural petroliferous zone, there develops an alternation of coastal-marine and marine environments, with a progressively increasing prominence of the marine at the bottom up, in the geologic section. Such is the pattern, a pattern of expression of the facies-lithologic base of our maps (Figs. 10, and 11). The history of sedimentation and the evolution of geographic environments in the Franian Age are given more thoroughly and in a greater detail in the series of four maps published in the Atlas of Facies-Lithologic Maps of the Russian Platform [2].

The map of the distribution of organic carbon in clayey "packets" of the Franian Tier (Fig. 8) was built on the basis of 101 analyses of composites representing 2039 samples of the clays. The C_{org} data on the map prove that the variations in the organic carbon content within the area are not accidental but are determined by the principles of zonations. The content of organic carbon is at its lowest, is not over 0.25% in the clayey horizons within the continental environments occupying the very large territory which embraces the northern, the northwestern, and the central areas of the Platform. The content of C_{org} increases away from this center, gradually, toward the east, the southeast, and the south, beginning to fluctuate between 0.25 and 0.50% already on the periphery of the Platform. The $\%C_{org}$, however, goes up to 0.50-0.75%, and, locally, almost to 1%, on the northwestern and northeastern slopes of the Voronezh massif and on the Tokma Roof (Tokma Svod). The 0.75% isograd forms the northern and southeastern boundaries of the Volga-Ural petroliferous zone. The content of C_{org} continues to rise to the northeast (of the boundaries), toward the core of the province, attaining several percent, even 6 to 7%, in places, in Tatariya and Bashkiriya.



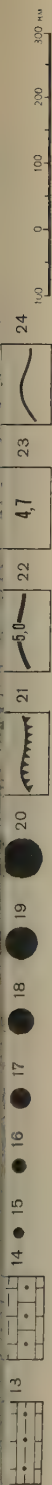


Fig. 9. Lithologic - geochemical map showing the content of disseminated organic carbon in carbonate rocks of the Upper Devonian, the Franian Tier, of the Russian Platform.

Key: Same as in Figure 8.

These relationships suggest more convincingly the existence of a direct connection between the amounts of organic substance disseminated in the Franian Tier and the regionally petroliferous character of this stratigraphic complex. The expressions of petroleum are found in the particular areas where the content of organic carbon attains its highest levels.

The map of distribution of $C_{org.}$ in carbonate rocks of the Franian Tier, based on the analyses of 84 composites representing 2768 samples (Fig. 9) is essentially a repetition of the $C_{org.}$

distribution pattern in the Franian clays. The differences here are due essentially to the displacement of the 0.25% isograd still farther east so that the entire northwest of the Platform, its center, and the northwestern slope of the Voronezh massif become areas in which the average content of $C_{org.}$ does not rise above 0.25%.

East of the Volga, however, there is an increase in the $C_{org.}$ and its 0.75% isograd envelopes the

Volga-Ural petroliferous province. Locally, in this province, the $C_{org.}$ content of carbonate rocks rises up to 1 and 2% and still higher.

The $C_{org.}$ distribution map for sandy "packets" of the Franian Tier, based on the analyses of 104 composites representing 1393 samples (Fig. 10) likewise preserves the fundamental features of the $C_{org.}$ distribution pattern in the clays. However, some of the essential details of the pattern are lost in the sands, because of their significantly lower $C_{org.}$ content. As in the previous cases, the Volga-Ural petroliferous province and the northeastern slope of the Voronezh massif are conspicuous by their somewhat higher content of organic carbon against the low general background of the Platform.

Our problem was to find out where there is any definite relationship between the organic carbon content of clays and their present geochemical environment. We know that, depending on effectiveness of the oxidation-reduction environments, there are changes in the state of





Fig. 10. Lithologic - geochemical map showing the content of disseminated carbon in sands of the Upper Devonian, the Franian Tier, of the Russian Platform.

Key: Same as in Figure 8.

oxidation of polyvalent chemical elements responding quickly to any oxidation-reduction shifts in the geochemical environments. Iron, a rock-forming oxide in the clays, is one of such elements. As a rule, iron is present both in its ferric and ferrous states. We determined both of these forms in all composites of the clays. This made it possible for us to calculate the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratios and to use the results as indications of the geochemical environments in the sediments. The higher this ratio, the more strongly oxidizing is the environment. The oxidizing intensity of the environment decreases in parallel to the falling $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio, until the ratio arrives at a certain threshold, apparently 1.0 or below, whereupon the environment acquires a stable reducing character.

The $\text{Fe}_2\text{O}_3/\text{FeO}$ ratios in clays of the Franian Tier were plotted on the facies-lithologic base map (Fig. 11). The following isograds were drawn, for the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratios in the sections: 10.0, 7.5, 5.0, 2.5, 1.5, and 1.0. The resulting pattern is an expression of a relationship between the areal distribution of the clayey "packets" (Fig. 8) and the concentrations of organic carbon in different geochemical environments (Fig. 11). Thus, for example, the northwest and the west of the Russian Platform are the zones of chiefly continental sediments bordering directly on the shore of the ancient sea and containing the minimal quantities of $\text{C}_{\text{Org.}}$. These sediments are within the 10.0 isograd on the map which is an indication of the marked preponderance of oxidizing environments in the area. The $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio decreases gradually from 10.0 to 5.0 toward the central parts of the Platform. The content of $\text{C}_{\text{Org.}}$ increases in the same direction. There

is a further decrease in the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio, from 5.0 to 1.0 to the east and the southeast from the center of the Platform accompanied by a corresponding rise in the $\text{C}_{\text{Org.}}$ content of the clays (Fig. 8). The 1.0 isograd encloses the northeastern slope of the Voronezh massif and the Volga-Ural petroleum province in which the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio falls below 1.0 defining thereby the region with a definite preponderance of

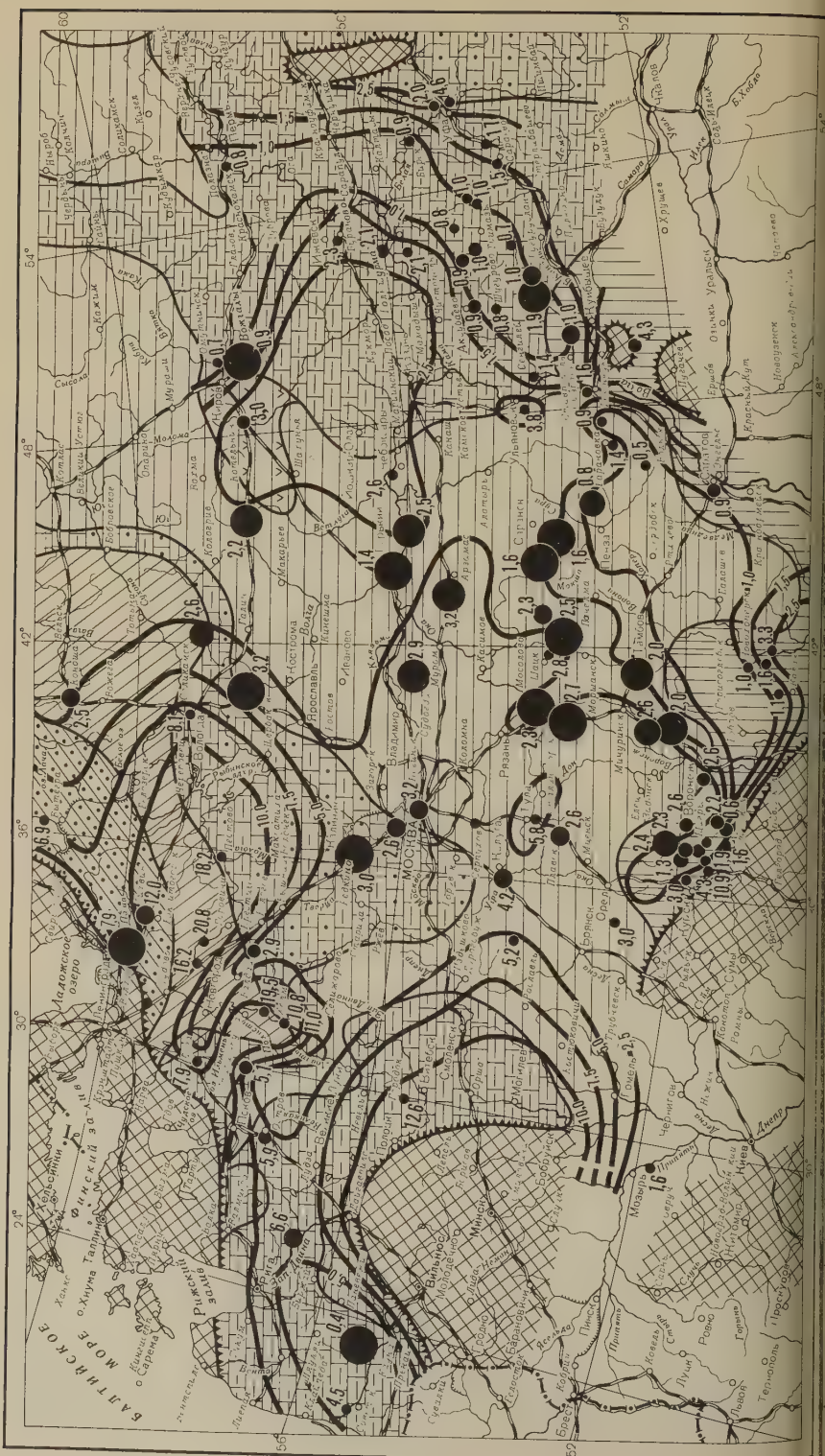




Fig. 11. Lithologic - geochemical map showing variations in the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio in clays of the Upper Devonian, the Franian Tier, of the Russian Platform.
Key: Same as in Figure 8.

reducing environments. It is in this region, as we had already seen, that the Franian clays contain the highest quantities of organic carbon (Fig. 8) and the sands of the Pashiisk Suite,* in the Volga-Ural region, are petroliferous economically.

The high content of organic carbon (Fig. 9) and the low $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio (less than 1) in the Franian clays of the northeastern slope of the Voronezh massif (Fig. 11) and of the Tokma Roof (Tokma Svod), together with the resemblance of their facies-lithologic sedimentation environments and the corresponding environments in the Volga-Ural petroleum province, to a certain extent, enable us (tentatively) to appraise these districts as being favorable for prospecting for petroleum.

The relationships here discussed leave no doubt that the higher concentrations of disseminated organic carbon were responsible for the regionally sustained and stable reducing environment in clayey sediments, which, in turn, determined both the course of the transformation of the bituminous fraction of the organic substance into oil and the valence-change of such an extensively distributed chemical element as iron.

The present work was carried out over a long period of time (1953 - 1958). In trips for the procurement of drillcores, descriptions of collections, calculations, preparation of composite samples, the following persons took part, in addition to the author: Z. N. Buyalova, M. N. Ilyukhin, G. A. Kazakov, N. F. Kopylova, M. I. Kuleshova, and Z. V. Khlebnikova. The analytical determinations of C_{org} took more than three years (1955-1958) and were conducted chiefly by members of the laboratory staff, V. P. Avraamova and Z. V. Khlebnikova. Determinations of the forms of iron were done by L. S. Dimitrieva, Laborant. Substantial aid was rendered by Z. V. Khlebnikova in the sta-

*The Pashiisk Suite (after the district of the same name, on the western slopes of Central Ural consists of Upper Devonian sands, silts, shales, and clays containing locally some concretionary iron ores.
VPS

tistical calculations, and by G. N. Kalenova in the preparation of the maps. The author considers it his duty to give his thanks to his comrades in the work.

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GEOCHEMICAL CHARACTERISTICS OF WEATHERING PROCESSES IN NEPHELINE SYENITES OF Khibina Tundra

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Abstract

The geochemical nature of the chemical weathering processes in the Khibina massif, where these processes are widely displayed and related to tectonic fracture zones, is given in this article in a new light. On the basis of the geological position of the fracture zones of break, the mineralogical composition and the experimental investigations of the solubility of the chief alkalic rock minerals, the author distinguishes two geochemical types of linear weathering crusts—in steep and in gently sloping zones. In spite of their similar age the chemical peculiarities of the mineral forming process are different in each zone. They are determined according to the ability of nepheline to hydrolyze in water, to the rate of surface water drainage, and to the difference in the solutions. In steep zones where the rate of water flow will be relative-ly high, the pH of the medium will be the lowest. In gently sloping zones, where the water may be almost stagnant, the pH can reach 11. These differences bring about in every type of the linear weathering crust, a typical minerals associa-

In the extensive literature dealing with the formation of the weathering crust, main attention is given to the chemical weathering of basic, intermediate basic, and acid rocks [B. Polynov, 11; P. A. Zemyatchenskii, 8; V. I. Vinzburg and I. A. Rukavishnikova, 2,3; V. P. Petrov, 10; G. S. Zolotarev, 4 and 5], and others. Successive alterations of rocks, conditions under which rocks are formed, stages in the alteration, physico-chemical factors conducive to weathering, stages of the formation of minerals, geochemical and other characteristics of origins of minerals, are the principal topics of the research.

Nepheline syenites were studied far less thoroughly from this point of view, particularly in the extreme north, in the environments of the Khibina Peninsula. The linear (fissure bound)* weathered crust discovered in the Khibina alkalic massif is undoubtedly interesting, for that reason, partly because it was possible, by means of mine workings, to follow and to trace this type of weathered crust and to prove the super-genetic origin of these formations, as well as to disentangle the sequence of formation of minerals in the linear weathered crust, while making

* "reshchinnaya (treshchinnaya)" is translated as "linear (fissure-bound)." VPS

it possible at the same time to collect additional materials so as to broaden our view of the character and of the geochemical environment in which the linear weathered crust had developed in nepheline syenites.

The linear weathered crust was studied most fully in the Yukspor railway tunnel through the Yukspor Mountain, practically across the entire jacupirangite-urtite series of rocks, as well as in mine workings at different levels in the Yukspor, the Kukisvumchorr, and a part of the Rasvumchorr apatite-nepheline mines.

We should note here that chemical weathering was imposed not only on the ijolite-urtites but also on the accumulations of apatite-nepheline ores, on pegmatites, including their various mineralizations, and on hydrothermal formations. In the present discussion of the formation of minerals in the linear weathered crust, we shall limit ourselves to alterations of the principal rock-forming minerals: nepheline, aegirine-augite, apatite, and sphene, which determine the characteristics of the linear weathered crust in nepheline syenites.

A BRIEF OUTLINE OF PETROGRAPHY

The ijolite-urtite intrusion is one of the terminal differentiates of the Khibina massif of nepheline syenites [B. M. Kupletskii, 9; N. A. Eliseev, 7] having a ring-like structure in its plane. The arc-like intrusion dips 30° toward the core of the massif. In the hanging wall of Yukspor Mountain, the host rocks are poikilitic nepheline syenites (rischorrites); on the footwall the host rocks are coarse-grained khibinites. Accumulations of apatite* are associated with contacts between the rischorrite and the Jacupirangite-urtite rock series.

Fine-grained ijolites containing abundant [porphyritic] grains of nepheline (isometric and rarely idiomorphic in shape, up to 5 mm in diameter) are present in the khibinite contacts, in the khibinite-rischorrite traverses through the rocks of the complex. As we go deeper into the massif, the grain size of the matrix of the rocks increases up to 3-4 mm, whereas the porphyry-like grains increase up to 8-10 mm in diameter. Alternations of rocks containing fine or coarse porphyry-like grains are fairly common but irregular. Their proportions in the rocks tend to decrease away from the contact, and they practically disappear about 300 meters from the contact. Within this span, and farther, among the medium-grained ijolites, there are isolated bands of melteigite, jacupirangite, and even urtite, containing up to 90% nepheline. The turn of the tunnel, near its middle (1200 m. from the khibinites) coincides with the transition to the coarse-grained urtites of the hanging wall of the intrusion with the host rocks. In this span, and farther north among the urtites, there are branches of an immense

*Our earlier publication [M. D. Dorfman, 6] describes a surficial petrographic traverse through Yukspor Mountain roughly in the direction of the tunnel.

natitic body the whole of which is traversed by another tunnel, parallel to the main tunnel,* at the distance of some 500 m. Near the upper contact, the coarse-grained urtites alternate repeatedly with lens-like layers of banded fine-grained ijolites up to 10 cm thick. Their banded character depends on the regularly distributed dark fine-grained lenses and spots measuring 1 to 5 cm in diameter and up to 20 cm in length.

The clearly defined trachytoid character due to the linear orientation of the feldspars is typical of the entire rock series, with the exception of the coarse-grained urtites, in which it is absent.

THE LINEAR WEATHERED CRUST

The formation of minerals in the decomposed zones of the Khibina mafic rocks was treated so far as if it were a hydrothermal process [N. P. Chirvinskii, 12; Yu. V. Nikitin.**]. The possibility that some of the Khibina clay minerals are formed by chemical weathering was recognized first by P. A. Zemyatchenskii [8], who discovered flour-like accumulations, resembling flour, in some specimens of nepheline syenites. Later, in 1950-1954, E. I. Semenov** discovered certain supergene minerals in the Khibina and in the Lovozero Tundras, and M. M. Yashina**, in the Lovozero, determined zeolitization of the rocks under the influence of supergene processes. Although all of these uncorrelated facts were undoubtedly interesting, they were not sufficient by themselves as premises for an appraisal of the factors determining the environments determining formation of the minerals. Only systematic studies of minerals in the decomposed zones enabled us to recognize the extensive development of chemical weathering in nepheline syenites.

Twenty-two tectonic zones were identified in the Yukspor Tunnel in which the fragmented rocks had been subjected to a severe weathering. The thicknesses of these zones fluctuate between 50 meters and 10 centimeters. The largest are in the southern part of the tunnel by the foot of the intrusion. The preponderant orientation of these zones is at 70°, coinciding with the orientation of valleys and gorges. The weathered tectonic zones are almost unrecognizable at the surface of the ground, because of their poor exposures. Their presence is suggested only by isolated patches of ferruginized rocks or by narrow depressures, 10 meters deep, and deeper, visible on the narrow and steeply sloping or in the isthmuses† between glacial cirques. The rocks

* "Shtol'no-Khodovaya shtol'nya" is translated as "the main tunnel"; the term "shtol'" means "the tunnel used for transport and communication." VPS translation. Files of the Kola Branch of the Academy of Sciences of the USSR. † "Istmychka," "overlock," is translated as "isthmus." VPS



Fig. 1. The Rasvumchorr Mountain. A gaping fissure formed by erosion of products of weathering.

in these tectonic zones are so thoroughly altered that their physical weathering and erosion are very easy in surficial environments (Fig. 1).

Two types of the linear weathered crust are differentiated, depending on the geologic position of the decomposed rocks: the steeply dipping and the gently dipping types (60 to 90° and 0 to 30° respectively). The steeply dipping type is far more common and is characterized by its great thickness, locally, with "blow-outs"*. This type consists, as a rule, of several closely spaced bands separated one from another by relicts of unaltered rocks. The gently dipping type is generally a system of branching fissures joined not uncommonly with fissures of the steeply dipping type. The gently dipping type is characteristically narrow (thin), thinning out with depth. It was practically impossible to follow the fissure zones through their entire dip. The tunnel, however, cut through the mountain (at an angle), with a difference in elevation of 500 m. serves, as it were, as a means of exposing such zones at different hypsometric levels. At the surface of the ground at the entrance to the tunnel there are exposures of the linear weathered crust in its upper sections. As the tunnel sinks deeper into the mountains, it exposes the deeper sections of the weathered crust and even, in part, its roots.

In the steeply dipping zones by the entrance to the tunnel the rock is bleached, loosened, and altered beyond recognition. The rock is chiefly white hydromica impregnated locally with a fine mixture of hematite and chalcedony. Earthy anatase and accumulations of white chalcedonic quartz, up to 20 cm in diameter, are also there. Such

*That is, by local expansions in all dimensions. VPS

the amounts of quartz are already absent in the deeper sections of the crust exposed in the tunnel. Colors of the altered rocks exposed in the tunnel change with depth as the rocks become more brown because of the increasing proportion of hydrohematite or limonite. Still deeper, rocks of the fissure zones are somewhat lighter in color, and greenish, because of the nontronitization of their pyroxenes. Thus, in the mica, a hydrohematite-chalcedony mixture, and nontronite are the principal minerals in the linear weathered crust of the steeply dipping type.

Montmorillonite, locally with chalcedony spherulites, is preponderant in the upper parts of the gently dipping crust near the surface of the ground. Farther in depth, beidellite makes its appearance, followed by celadonites, all of which are intimately associated with montmorillonite and beidellite. Reniform crusts and veinlets of francolite are found at the same depths, where the linear weathered crust lies in vicinity of the small accumulations of apatite-nepheline ores. Thus either one of the weathered crust types is characterized by its own diagnostic assembly of minerals. We are not reporting here the products of weathering of accessory minerals (for example, zirfesite, zirsite*, catapeite, and mon eudialyte), because of their minor value in the present study.

SOME DATA ON CONDITIONS OF FORMATION OF MINERALS IN WEATHERED CRUST

In the present study we use extensively both geologic and field data in connection with the origins of minerals related to the weathering process. Inasmuch as supergene minerals are formed at ordinary temperatures and pressures, many of them could be synthesized under conditions approaching natural ones. Without repetition of the findings already published in this problem, we shall merely report on some of our own results with nepheline syenite minerals.

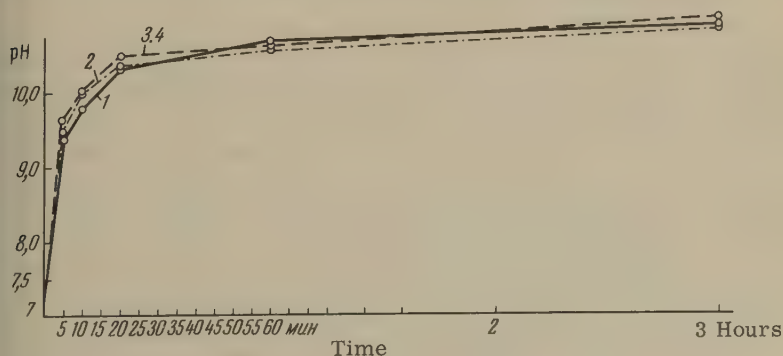


Fig. 2. Changes in pH of medium by solution of nepheline in distilled water. Experiments in quadruplicate.

cannot identify this mineral. VPS
listed in English mineral indexes. EWH

Experiments with solubility of nepheline in distilled water (pH 7.1 at 16°C; solid; liquid ratio 1:2) showed that the pH of the liquid phase attains its highest alkalinity within 3 hours (Fig. 2). The same is the case in the experiments with hackmanite.

The solubility of nepheline in water, under the same conditions, may be appraised by the following data (Fig. 3):

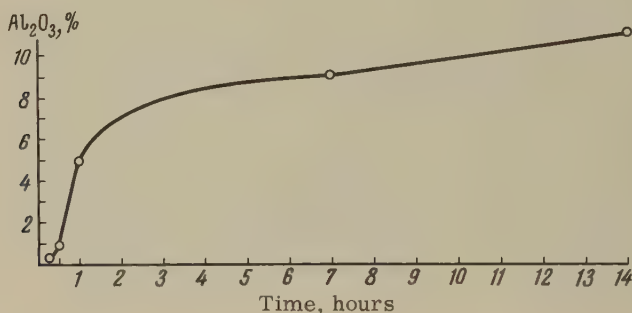


Fig. 3. Leaching-out of Al_2O_3 from nepheline by distilled water.

Solution of the mineral proceeds at a rapidly increasing rate during the first hour, whereupon solution becomes gradually retarded and tends to approach the concentration of Al_2O_3 determined by solubility of the mineral.*

Thus alkalinity of the leachates develops only at the expense of nepheline or of hackmanite. Alumina and silica pass into solution as the result of leaching of nepheline.

In our experiments with apatite, it was necessary for us to verify Britton's results [1], according to which the precipitation of calcium phosphates at pH 7 is characteristic of these salts. When finely ground apatite was shaken with distilled water for 40 minutes (solid: liquid as 1:1 at 16°C), pH of the solution was up to 7.62 and the filtrate was found to contain 0.07 grams P_2O_5 per liter. The pH went up to 8.1 after the addition of a small amount of nepheline to the mixture, and the apatite became insoluble, for no P_2O_5 could be detected in the filtrate. The solubility of apatite is limited therefore by the pH of the solution.

Experiments with sodalite containing hackmanite and sulfur indicated that, following the water-mineral interaction, the oxidation-reduction potential (Eh) of this mineral is much lower than of other minerals

*The meaning of this paragraph is: The leaching of alumina out of nepheline is very rapid during the first hour of the experiment but becomes retarded gradually later, as the concentration of Al_2O_3 in the leachate tends to approach the limit of its solubility in water, under the experimental conditions. VPS

the rock: nepheline, pyroxenes, feldspar. For example, the Eh = mv. directly after wetting of hackmanite with water going up to mv. after 24 hours. The Eh of nepheline is ± 235 mv. but is up to 2 mv. after 24 hours. Thus the low oxidation-reduction potential of the weathering of rocks containing hackmanite depends on the sulphate constituent of this mineral. Since the distribution of hackmanite is highly irregular in the rocks, its Eh effect may be only local, where drainage is poorly developed.

GEOCHEMICAL CHARACTERISTICS OF WEATHERING PROCESSES

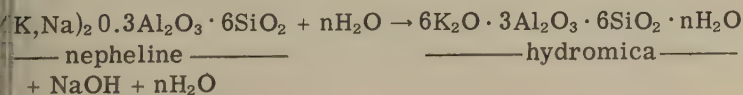
The geologic position of the linear weathered crust, comparisons between profiles through the fissure zones at different levels of the deposit and the tunnel, and our experimental studies enable us here to present a general pattern of the evolution of weathering processes in the jacupiritingite-urtite series of rocks. The physico-chemical environment plays an essential role in the development of weathering processes, alongside the decisively important geologic factors. This environment is defined by the mineralogic composition of rocks, by the capacity of the minerals to hydrolyze in water, by the rate of drainage, and by the state of fragmentation of the rocks. In the steeply dipping type of linear weathered crust, the rate of the downward movement of the surface water will be at its highest, while their pH will be relatively low, in the vicinity of 9 (as shown by direct measurements of the pH of waters in steeply dipping zones). In the gently dipping type of the crust, the waters will be almost stagnant, and consequently the pH may be as high as 11. In gaping cracks, on the other hand, even in direct proximity to the fissure zones, the pH of waters is 6.5 to 7 at 300 meter depths.

Every type of linear weathered crust has its own specific features of development, as may be seen from the foregoing considerations.

Weathering Processes in Steeply Dipping Fissure Zones

Four successive stages, each with its own specific characteristics, may be distinguished in the development of the steeply dipping type of linear weathered crust.

Stage I (Hydromica). This stage is characterized by the formation of hydromica on nepheline. The decomposition of nepheline may be expressed by the following reaction:



The leaching out of Na causes an increase in alkalinity of the solution. K, Al, Si are re-grouped and remain in place, as hydromica. Sodium becomes replaced by oxonium (H_3O^+), on prolonged leaching;

the amounts of oxonium are up to 20%, and higher, near the surface but decrease down to 2-3% in depth. There are corresponding changes in colors of the mineral toward the surface: green → pink → white.

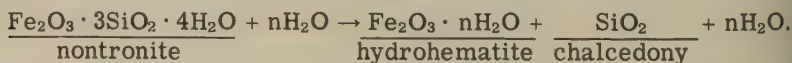
Hydromica may be transformed into beidellite, as the result of a prolonged and retarded leaching, as, for example, in the intermediate type of the linear weathered crust (dipping at 40 to 45°) near the surface.

Stage II (nontronitic) is characterized by the replacement of aegirine-augite by nontronite. The original structure of the rock is preserved in some of the sediments; the original contours and shapes, by some of the rock-forming minerals. The replacement of nepheline by hydromica is practically complete here, while pyroxene is transformed into an olive-green nontronite.

The conversion of aegirine-augite* into nontronite is represented in the following manner:
$$\frac{\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2}{\text{aegirine-augite}} + n\text{H}_2\text{O} \rightarrow \frac{\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}}{\text{nontronite}} + \frac{\text{SiO}_2}{\text{chalcedony}} + \text{NaOH} + n\text{H}_2\text{O}.$$

Chalcedony is formed alongside nontronite in the weathering of pyroxene. Alkalinity of the solutions is maintained by accessions of NaOH.

Stage III (limonitic) is characterized by the oxidation of nontronite and by the resulting formation of thin films of hydrohematite or limonite in a mixture with chalcedony or with chalcedony-quartz. The rock loses its original structure entirely and becomes brown. The lateration of nontronite proceeds according to the reaction:



Stage IV is characteristic of the linear weathered crust only when this crust is near the surface of the ground. This stage is essentially the same "limonitic" one, except that it is accompanied by appreciable accumulations of porcelain-like or dark-brown chalcedonic quartz. It is distinguished also by a general bleaching of the rock, the highest percentages of oxonium in the hydromica, and a re-deposition and accumulation of hydrohematite in isolated parts of the rock.

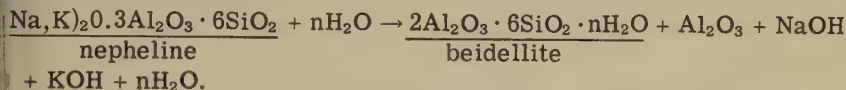
(b) Weathering Processes in Gently-Dipping Fissure Zones.

The following three stages are recognizable in the development of the gently dipping type of the linear weathered crust.

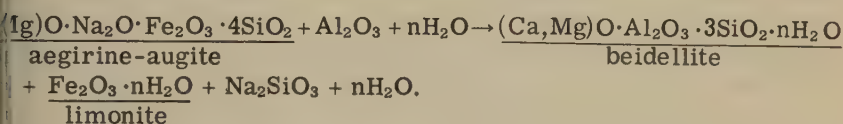
Stage I (beidellite-montmorillonite-zeolitic) is characterized by the

*Up to 8% MgO and CaO is present invariably in aegirine-augite. These oxides are not always included in our statements of the reactions, for the sake of clarity. They play a substantial part in the weathering of rocks in the gently dipping type of the linear weathered crust.

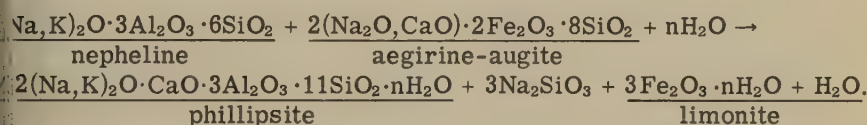
ation of clay minerals and of zeolites after nepheline and pyrox-. On weathering of these minerals, nepheline is the first one to be ected to alteration, because it hydrolyzes in water more easily the others. The alteration of nepheline into beidellite may be represented by the following reaction:



ne weathering of aegirine-augite into beidellite takes its course in following reaction:

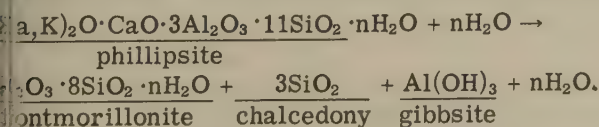


ne concurrent weathering of nepheline and aegirine-augite favors formation of phillipsite and thomsonite (zeolites); the formation of needle hair-like natrolite is observed more rarely. Zeolitization of rock takes place according to the reaction:

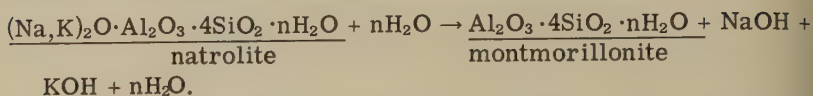


on hydroxides, formed by the weathering of pyroxene, are commonly precipitated as a bright brown-red band on beidellite in the final parts of the zone. The invariable presence of montmorillonite in the central parts of the linear weathered crust may be due to instability of beidellite and to its conversion into montmorillonite, and product of the weathering. The zeolites are accumulated in places either at the beidellite-montmorillonite boundary or else in montmorillonite itself, where small clusters of phillipsite and thomsonite are found either in cavities within montmorillonite or as growths on montmorillonite.

age II (*beidellite-montmorillonitic*) is characterized by a replacement of zeolites by montmorillonite, with the quantities of zeolites decreasing toward the surface. On weathering of the zeolites gibbsite is formed alongside montmorillonite, together with spherulites of chalcedony whose core, as a rule, is montmorillonite. phillipsite is weathered according to the following pattern:



The weathering of natrolite* is somewhat different:



The absence of certain chalcedony-montmorillonites and of later gibbsite in this group of minerals may be explained by the weathering of natrolite.

Stage III (Montmorillonitic) is characterized by a transition from beidellite to montmorillonite. This process is connected with a certain re-grouping of the mineral structures, with the accompanying change in the $\text{Al}_2\text{O}_3 : \text{SiO}_2$ from 1:3 to 1:4.

Francolite is the diagnostic mineral for the gently dipping type of the linear weathered crust. It is formed, in such environments, only where fissure zones are overlain by apatite-nepheline rocks.

DEVELOPMENT OF LINEAR WEATHERED CRUST IN NEPHELINE SYENITES**

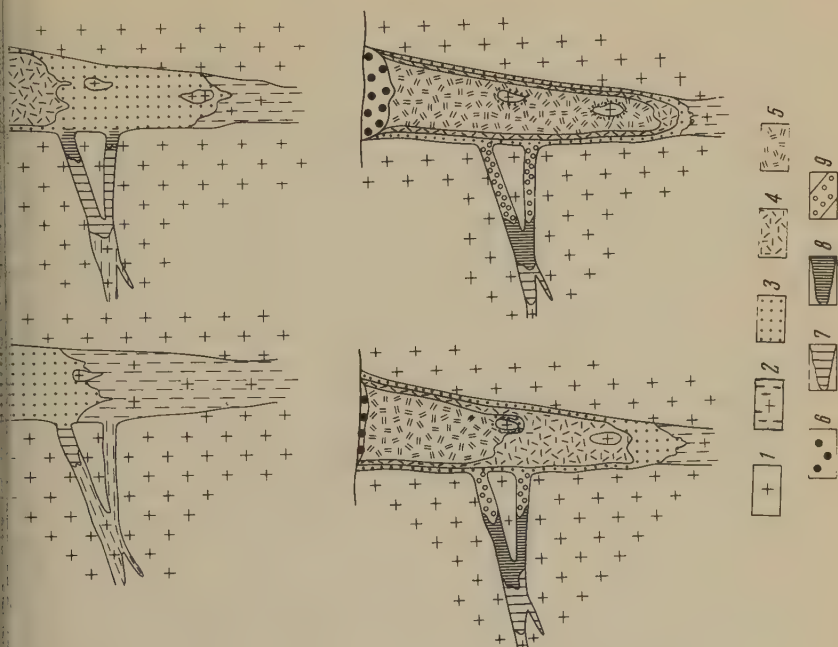
Either one of the types of the linear weathered crust has its own geochemical characteristics, as may be seen from the description of processes involved in the chemical weathering, although both types are of the same age. As already stated, these distinctions are due to several factors and, first of all, to nepheline, the principal rock-forming mineral. Field observations as well as experimental data show that nepheline hydrolyzes easily and may produce solutions at very high pH levels (i.e. at highly alkaline pH-VPS), under favorable conditions. The pH is a decisive factor in the mineral-forming processes of the linear weathered crust. Depending on the rate of drainage of the surface waters, the pH of the liquid phase varies over a certain range, and it is these variations that determine the characteristic complex of minerals in either one of the types of the linear weathered crust.

Among the characteristics of the weathering of ijolite-urtites, unlike the weathering of acid and basic rocks, we should note the stability of feldspar. Feldspar always remains fresh throughout all of the stages of weathering of ijolite-urtites and of their pegmatites and only locally shows a little darkening.

Four stages are recognizable in the development of the linear weathered crust (Fig. 4). The first and the initial stage (from the surface down), along the dip of steeply dipping fissure zones, is characterized by the formation of hydromica after nepheline while all other minerals of the rock remain entirely stable. Such selective weathering of nepheline results in a leaching out of Na, the most mobile of the alkali metals, by flowing waters, while potassium, together with Al and Si, is regrouped into neomorphs.

*In the original "nontronite"; misprint; corrected. VPS

**In the original: "Peculiarities in the Development of the Crust of Weathering in Nepheline Syenites." VPS



Pattern of development of linear weathered crust in nepheline syenites. Stages: 2—fissure zones; four stages in the development of weathered crust in gently dipping fissure zones; 3—hydromicaceous; 4—nontronitic; 5—limonitic; 6—chalcedony; three stages in the development of weathered crust in gently dipping fissure zones; 7—beidellite-montmorillonite-zeolitic; 8—beidellite-montmorillonitic; 9—montmorillonitic.

Unidirectional and continuous movement of the leaching waters conducive to developments of alkaline pH and, even on the contrary, tends to produce more acid pH, in the long run, whereupon begins a gradual replacement of the K in the mica by oxonium. In gently dipping zones, where waters are practically stagnant and the medium is most highly alkaline, beidellite, zeolites, and montmorillonite develop. This latter process is characterized by an eventual concurrence in time, of the weathering of all of the rock-forming minerals, with the resulting developments of beidellite, montmorillonite, various zeolites, gibbsite, chalcedony, francolite, and others. These minerals are precipitated in an entirely definite sequence which is a direct function of the physico-chemical properties of the medium. For example, gibbsite, a K, Na, Ca mineral, is the first one, among the zeolites, to appear and it is followed by thomsonite, a Ca, Na min-

The process of weathering develops progressively into depths of the crust. If, in its second stage, begins gradually in the upper parts of the weathered crust. In steeply dipping zones, in places where

nepheline was already replaced by hydromica and where the pH has already changed, aegirine-augite begins to be replaced by nontronite. In gently dipping zones, the zeolites become unstable and are converted into aggregations of montmorillonite, gibbsite, and chalcedony.

The third stage, in steeply dipping zones, is characterized by an alteration of nontronite and by the development of hydrohematite (or limonite) after nontronite, together with chalcedony. The process develops more rapidly than the formation of nontronite. This serves to explain the presence of only small amounts of nontronite relicts even at appreciable depths. In environments where nontronite becomes ochreous, i.e. in relatively acid environments, there begins a weathering of sphene into an earthy variety of anatase. The first two stages extend to greater depths, in gently dipping zones, where beidellite begins to be transformed into montmorillonite. In the course of time, the space still enveloped by the earlier stages of the weathering grows smaller, while montmorillonite—the end product of the weathering—takes over.

The fourth stage, recognizable only in steeply dipping zones, differs from the third only in some of its sections near the surface, where large accumulations of chalcedonic quartz may be seen among the light colored hydromica.

The formation of francolite,* $\text{Ca}_{10}\text{P}_5\text{CO}_{24}(\text{OH},\text{F})_2$ is one of the most interesting features of the weathering stages of nepheline syenites here described. As already stated, francolite is the characteristic mineral of the gently dipping type of the linear weathered crust wherein it is formed in montmorillonite-zeolite aggregates only in places where the fissure zone is overlain by rocks rich in apatite. This limitation determining the formation of francolite is due to a certain change in the pH of the solutions, in definite geologic environments, in the initial and also in the subsequent stages of their descent. Our experiments with solubility of apatite led to the conclusion that the decomposition of this mineral takes place at pH not higher than 8. With this consideration in mind, we may represent the formation of francolite as follows:

The originally neutral or almost neutral surface waters passing through apatite-bearing rock dissolve some apatite in their course. As alkalinity of the percolate increases rapidly, because of the solution of nepheline, the solution of apatite becomes inhibited. If the descending waters, at moderate pH, having already passed through an apatitic body of rock, happen to reach a gently dipping fissure zone, where the environment is alkaline, a precipitation of francolite is the result. The alkaline character of the medium is therefore the limiting factor in the formation of large quantities of secondary calcium phosphates and is consequently responsible for the scarcity of these minerals in the Khibina.

In places where a gently dipping fissure zone intersects hydrothermal veins filled with natrolite, the natrolite at their contact, within a 5 mm span, changed into montmorillonite. Hydrothermal veins of the

*Francolite is discussed in a separate publication by the author [13].

alkalic massifs differ markedly from supergene veins both in geologic position and in their morphologic and paragenetic characteristics. Hydrothermal zeolites form thin (2 to 3 mm) single-mineral veins in steeply dipping fissures and in unaltered ijolite-urthites. These veins consist of a dense, slab-like, coarse-grained, semi-transparent natrolite. As a rule, they are free from the near-vein alteration. As a contrast, supergene zeolites are associated most closely with clay minerals, limonite, and francolite. Moreover, they are invariably only in the gently dipping type of the linear weathered

The linear weathered crust is characterized by its zoning. These bottom zones in the steeply dipping type are as follows: (a) a somewhat bleached rock containing chiefly hydromica with chalcedony-quartz and, locally, near the surface, with re-deposited hydrohematite; (b) the zone of hydromica, stained brown by iron hydroxides, altered nontronite and anatase; (c) the zone of greenish or pink hydromica, with fresh aegirine-augite, sphene, and relict structure of rock. The gently dipping type of the crust has the following sequence of zones, down the dip: (a) montmorillonitic; (b) beidellite-montmorillonitic; (c) beidellite-montmorillonite-zeolitic.

As previously stated, not only the thickness, but also the intensity of the weathering process are subject to changes with depth. By way of an example, we may refer to one of the steeply dipping zones of the Kukisvumchorr, where the zone separates into two branches, at 200 m below the surface, changes its shape, and finally wedges out at the 397 m. depth. A thinning of several zones is observed in the tunnel. The cessation of the weathering process in depth is illustrated by a steeply dipping zone intersected by a borehole. According to S. S. Kurbatov and A. F. Mikheeva, the percentage of hydromica (in this zone) changes with depth as follows: 17% at 105 to 106 m.; 15.1% at 106 to 108 m.; 6% at 156 to 157 m.; 7% at 180 to 197 m.

CONCLUSIONS

According to our findings, the processes of chemical weathering, as observed by the linear weathered crust, are developed extensively in the nepheline syenites of the Khibina massif.

The linear weathered crust develops in tectonic zones.

Chemical weathering takes place in tectonic zones with poorly developed drainage of surface waters. The weathering processes oriented in their direction by such zones may spread down to 500 m. and deeper, diminishing in their intensity and eventually wedging out.

We may distinguish two contemporaneous types of the weathered crust: the steeply dipping and the gently dipping ones.

The pH of the environment increases rapidly, because of the easy hydrolysis of nepheline in water.

5. Depending on the mineralogic composition of the rocks, the geologic positions of the fracture zones, and drainage, the resulting physico-chemical environments cause the formation of certain associations of minerals characteristic of the given type of the weathered crust, namely:

(a) potassium hydromica, nontronite, hydrohematite, limonite, anatase, chalcedony, and quartz in the steeply dipping type of the crust;

(b) montmorillonite, saponite, beidellite, zeolites (phillipsite, thompsonite, natrolite), gibbsite, chalcedony, francolite in the gently dipping type of the crust.

6. Either one of the weathered crust types is characterized by its own zones which depend on the stages of the lateration of its minerals.

Stages of Weathering of the Principle Rock-Forming Minerals

(A) Nepheline

↓
hydromica

↓
beidellite

↓
montmorillonite

↓
montmorillonite and zeolites
(phillipsite, thompsonite, natrolite)

↓
montmorillonite, gibbsite, and
chalcedony-montmorillonite

(B) Aegirine-Augite

↓
nontronite

↓
hydrohematite, gibbsite, and SiO_2
sphene
↓
anatase

↓
beidellite, limonite, and SiO_2

apatite
↓
francolite

7. The association of francolite only with the gently dipping type of the weathered crust below the apatite-nepheline rocks makes it perfectly clear that its source of phosphorus is the overlying accumulations of apatite rocks whence the phosphorus is leached by descending waters.

8. The supergene origin of zeolites (phillipsite, thompsonite, natrolite) is proved by their close association with beidellite, montmorillonite, francolite.

9. At the intersection of the gently dipping weathered crust and natrolite veins of hydrothermal origin, there develops a contact zone in which natrolite is replaced by montmorillonite.

10. The feldspar in ijolites-urtites and in their pegmatites remains always fresh, in contrast with the weathering of acid and basic rocks.

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THALLIUM IN ORE MINERALS OF THE VERKHNYAYA KVAISA

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Abstract

The thallium abundance in the chief ore minerals of the Verkhnyaya Kvaissa galena, sphalerite and marcasite has been studied. The colloform marcasite and sphalerite are relatively enriched in thallium ores the coarsely crystalline galena is impoverished in it. This may be explained by the peculiarity of ore deposits from colloid solutions. In the process of recrystallization of the gels of galena the latter may to some extent purify itself from captured impurities. Probably such self-purification accounts for the appearance of a thallium mineral—the hutchinsonite. A correlation of thallium and arsenic in galena and an antipathetic behavior of arsenic and antimony in case of a compensation replacement of lead by thallium is noted.

A large but not always reliable body of data on the distribution of thallium in different minerals has been accumulated by this time. The low reliability of some of the data on different minerals is due chiefly to the insufficiently reliable analytical procedures of the analyses, most of which are essentially qualitative or semiquantitative appraisal of the thallium content by the spectrographic method.

Results of such type make it difficult to form an opinion regarding the behavior of thallium in a particular process. Despite the fact that thallium is typically chalcophile, with the 18-electron outer shell of its ion, by virtue of its position in the periodic table, it is known, in greater detail, as typically lithophile in processes where it accompanies K, Rb, Cs, as reported by Ahrens [1, 2], Shaw [3], and others [4]. Thus the behavior of thallium as a sulfide element is not very well understood in many instances. We are not able to give a satisfactory explanation of the presence of thallium in many sulfides—pyrite, marcasite, sphalerite—and we know even less about the forms in which it is present in these minerals. It has been reported that thallium "highs" are associated with meta-colloidal and colloidal states of pyrite, marcasite, and sphalerite, which may be related, in turn, to the relatively high sorption capacity of the gels of these sulfides precipitated from their colloidal solutions [5].

As to the presence of thallium in galena—this problem is relatively more easy. Thallium resembles lead, its neighbor in the periodic table in many respects. A thallium-lead isomorphism is entirely feasible, because of the similar size of their polarized ions in sulfides. It is

ed also that the thallium-antimony or the thallium-bismuth as-
 tion, relatively common in galena, is due to a replacement of two
 ions by either $Tl^{+} - Sb^{3+}$ or $Tl^{+} - Bi^{3+}$ couple [5].

believe that further detailed studies of thallium parageneses in
 es may serve, to some extent, to clarify certain aspects of the
 or of thallium in hydrothermal processes, if we apply the exact
 tative methods in the analysis of certain geologically significant
 materials for thallium. With this purpose in mind, we undertook
 y involving the characteristic features of the distribution of
 um in the principal minerals of the Verkhnyaya Kvaisa.

gle-mineral samples of galena, sphalerite, and marcasite were
 from specimens of the ore collected down the dip and along the
 of the ore body. Thallium was determined colorimetrically, by
 brilliant green" method [6], in 0.5 g. aliquots of the samples.

The Verkhnyaya Kvaisa lead-zinc deposit is situated on the southern
 of the Main Range of the Caucasus, in Southern Osetiya. It is
 ated with a major fissure in porphyries of the Baios Suite (Jur-
 Middle Division, Tier 2, from bottom). The vein strikes almost
 west; its dip is to the south and is nearly vertical. The thickness
 ore body is irregular, both down the dip and along the strike.
 vein is relatively rich along its hanging wall (north) and relatively
 at its footwall (south). The mineralogical composition of the ores
 ple. The principal ore minerals are galena and metacolloidal and
 form sphalerites; the accessory minerals are pyrite and marcas-
 ry rare ones are arsenopyrite, chalcopyrite, and native silver.
 is predominant in the gangue; quartz, chalcedony, and zeolites
 present in subordinate quantities.

ere are variations in the mineralogic composition and in the tex-
 of the ore from the upper to the lower horizons. The middle hori-
 contain abundant nest-like secretions of crystalline galena in en-
 s of zoned sphalerite. Pyrite is unimportant in these horizons,
 it is present in the form of very small inclusions. Banded ores
 abundant in the upper horizons, and there is more pyrite and mar-
 in the ore mass. Preponderance of colloform over crystalline
 al structures is a major characteristic of the Verkhnyaya Kvaisa
 an indication of their deposition from colloidal solutions.

must report here an additional feature of the Verkhnyaya Kvaisa
 their carbonate character by which they are distinguished from
 ore common quartz-polymetallic or barite-polymetallic ores of
 rucassus.

re ore minerals are characterized by their thallium "highs".
 element was first detected in them spectrographically, by N. M.
 roenko (1947) and T. V. Ivanitskii [7]. Later on it was determined
 cally in several samples [5]. There were no systematic studies
 distribution of thallium in the minerals by any of these investi-

le 1 shows our data on thallium in the minerals, in the ores, and
 concentrates from the ore-dressing plant. On the basis of these

Table 1. Thallium in Ore Minerals of Verkhnyaya Kvaisa

Sample No.	Source	Mineral	% Tl
31	Tunnel 11	Sphalerite	2.4×10^{-4}
35	Tunnel 4	Sphalerite	9.0×10^{-4}
22	Tunnel 5	Sphalerite	4.2×10^{-4}
21	Tunnel 5	Sphalerite	7.8×10^{-4}
61	Tunnel 6	Sphalerite	7.5×10^{-4}
56	Tunnel 6	Sphalerite	7.0×10^{-4}
57	Tunnel 6	Sphalerite	7.0×10^{-4}
38	Horizon 1	Sphalerite	1.6×10^{-4}
39	Horizon 1	Sphalerite	5.0×10^{-4}
45	Horizon 11	Sphalerite	6.0×10^{-4}
26	Tunnel 2	Galena	1.8×10^{-4}
49	Tunnel 4	Galena	1.8×10^{-4}
20	Tunnel 5	Galena	7.8×10^{-4}
21	Tunnel 5	Galena	4.2×10^{-4}
22	Tunnel 5	Galena	1.0×10^{-3}
16	Tunnel 5	Galena	1.6×10^{-4}
65	Tunnel 6	Galena	3.0×10^{-4}
66	Tunnel 6	Galena	2.6×10^{-4}
77	Tunnel 6	Galena	3.6×10^{-4}
2	Tunnel 6	Galena	1.2×10^{-4}
3	Tunnel 6	Galena	3.4×10^{-4}
4	Tunnel 6	Galena	3.4×10^{-4}
55	Tunnel 6	Galena	4.0×10^{-4}
56	Tunnel 6	Galena	5.0×10^{-4}
57	Tunnel 6	Galena	6.0×10^{-4}
38	Horizon 1	Galena	2.2×10^{-4}
39	Horizon 11	Galena	5.0×10^{-4}
45	Horizon 11	Galena	2.8×10^{-4}
47	Horizon 111	Galena	1.0×10^{-4}
16	Tunnel 5	Marcasite	5.8×10^{-3}
80	Tunnel 6	Marcasite	6.4×10^{-3}
81	Tunnel 6	Marcasite	5.6×10^{-3}
23	Tunnel 11	Oxidized Ore	none
24	Tunnel 11	Oxidized Ore	none
Crude ore at ore-dressing plant			1.1×10^{-3}
Crude ore at ore-dressing plant			5.5×10^{-4}
Lead concentrate; July 1956*			1.6×10^{-3}
Zinc concentrate; July 1956*			1.8×10^{-3}
Lead concentrate; 1 wk., Aug. 1956†			2.4×10^{-3}
Zinc concentrate; 1 wk., Aug. 1956†			2.4×10^{-3}

*Probably monthly composites. VPS

†Probably weekly composites. VPS

results, we attempted to show the distribution of thallium in the ore minerals down the dip (Table 2) and along the strike of the ore body (Table 3). The tables include the data on thallium in minerals taken from the core of the vein where the mineralization is richest.

Table 2. Variations in Thallium Content of Galena and Sphalerite on Dip of the Ore Body

Western Section			Eastern Section		
Sample	Galena	Sphalerite	Item No.	Sample	% Tl in Galena
31; 1750m.	--	2.4×10^{-4}	8	49; 1660m.	1.8×10^{-4}
26; 1710m.	1.8×10^{-4}	--	9	20; 1620m.	7.8×10^{-4}
35; 1660m.	--	9.0×10^{-4}	10	55; 1580m.	4.0×10^{-4}
3; 1580m.	3.4×10^{-4}	--	11	56; 1580m.	5.0×10^{-4}
38; 1540m.	2.2×10^{-4}	--			
45; 1500m.	2.8×10^{-4}	6×10^{-4}			
47; 1460m.	1.0×10^{-4}	--			

3. Variations in Thallium Content of Galena Along Length of the Ore Vein

No.	77	2	3	4	56	57	55
	3.6×10^{-4}	1.2×10^{-4}	3.4×10^{-4} (450m.)	5×10^{-4}	5×10^{-4}	6×10^{-4}	4×10^{-4}
West				→ East			

indicated by the tables, there is very little change in the thallium content down dip and along the strike of the vein, despite a certain tendency toward an enrichment of thallium in the minerals from the middle horizons of the deposit. This tendency harmonizes with the general trend in the character of the mineralization: the massive and the best ores are chiefly in the middle horizons, whereas banded and disseminated ores are preponderant both in the upper and in the lower horizons.

The same dependence is shown, if we follow the variations in the thallium content of galena in relation to thickness of the vein. As statistical data show, massive rich ores are on the hanging wall and in the core of the vein, and the disseminated ores are in the footwall. Table 4 shows the variations in thallium content of galena in two sections across the vein, which is about 3 meters thick; one may see that the thallium "highs" are in the galena of the massive ore. The impression is created accordingly to the effect that the behavior of thallium in the sulfide mineral-forming process is closely related to the behavior of lead and zinc—the principal mineral-forming constituents of the solutions. Apparently the same physico-chemical and other environmental factors that are so conducive to deposition of massive ores of lead and zinc are conducive also to the highest enrichment of the sulfides in thallium. This is indeed a probability, if we consider that the sulfides are deposited from colloidal solutions and that,

Table 4. Variations in Thallium Content of Galena in Traverses across Ore Vein

Item No.		% Tl in Galena		
		Footwall	Core	Hanging Wall
1	Western Section	2.6×10^{-4}	3.4×10^{-4}	3.0×10^{-4}
2	Eastern Section	4.2×10^{-4}	1.6×10^{-3}	7.8×10^{-4}

if so, the behavior of the admixed elements should be modeled by the behavior of the major elements.

In regard to the distribution of thallium among the Verkhnyaya Kva minerals, there is an interesting and a conspicuous detail: there is more thallium in sphalerite than in galena. As shown in Figure 1, 5 out of 7 samples of sphalerite examined by us have more thallium than is found in galena, which was isolated from the same samples of the ore.

This detail, the distribution of thallium between galena and sphalerite, is characteristic also for certain other deposits (Raibl, Vislokh) containing abundant colloform sphalerites. In the instance of the same polymetallic deposits, however, in which sphalerite was crystallized from true solutions, we observe a reverse relationship: galena is enriched by thallium, as against sphalerite (Tekeli, Sadon, East Sgid); the sphalerite contains little or no thallium [5]. Consequently, when galena and sphalerite are deposited from true solutions, the distribution of thallium between these two minerals is governed by crystallochemical laws and thallium is enabled accordingly isomorphously to replace lead in the galena crystal structure, by virtue of the similar size of the radii of polarized ions of thallium and lead and of the chemical resemblance between these two ions.

When the sulfides are deposited from colloidal solutions, however, the gels of lead and zinc sulfides have about an equal opportunity to capture (to co-precipitate) a whole series of the admixture elements, including thallium. The distribution of thallium between the sulfide minerals, in this latter case, may be affected significantly by the crystallization-capacity of the minerals. The more simple the crystal lattice, the greater is the crystallization capacity [8].

In harmony with this principle, galena, with its cubic lattice, assumes its crystalline structure nearly completely, whereas the bulk of sphalerite largely preserves its colloform structure. As the precipitated gels may undergo selective crystallization, they may be liberated in the process from their adsorbed impurities of different kinds. The impoverishment of thallium in galena from the Verkhnyaya Kva, as against the colloform sphalerite, may be explained by some such self-purification of galena in the course of its crystallization from a gel. As to the mechanism of the capture of thallium by the precipitating

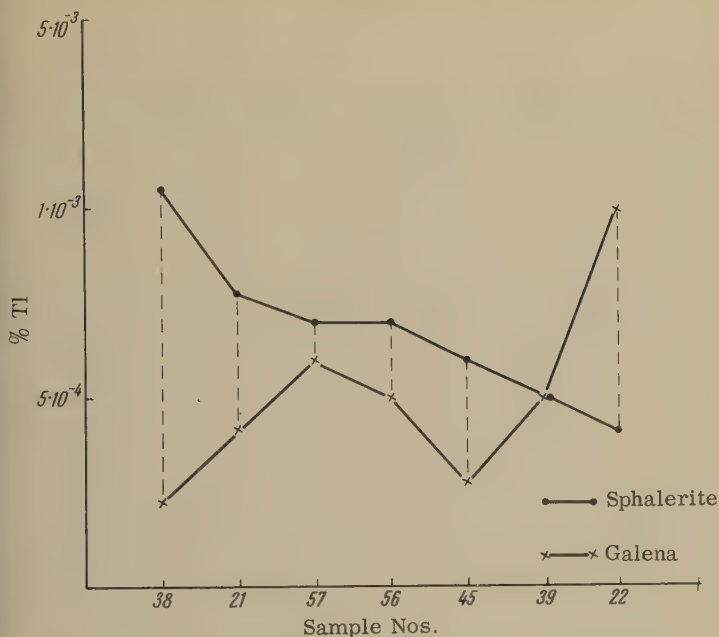


Fig. 1. Distribution of thallium in galena and sphalerite of Verkhnyaya Kvaisa.

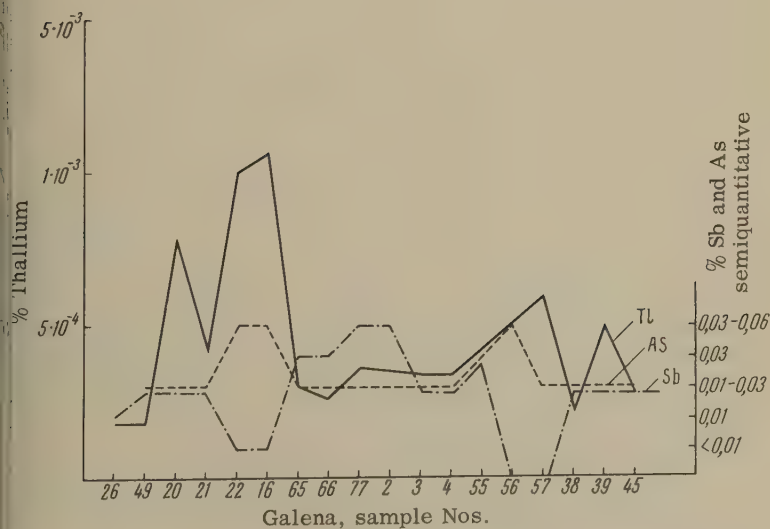


Fig. 2. Tallium-antimony-arsenic relationships in galena, Verkhnyaya Kvaisa (Dependence of thallium content on antimony and arsenic contents in galena of upper Kvaisa).

sulfides—the problem remains open and in need of an experimental study.

It should be especially pointed out here that an independent thallium mineral, hutchinsonite, was discovered in three specimens of sphalerite from the Verkhnyaya Kvaisa by S. S. Borishanskaya by the optical method [9]. A complete chemical analysis of this mineral was not feasible, because of its microscopic size. Chemically and spectrographically, nevertheless, "highs" of the hutchinsonite constituents—Pb, Cu, Ag, Tl—were detected in these sphalerite specimens. Since none of these elements is capable of replacing zinc isomorphously in sphalerite, their presence in the mineral should be attributed to their sorptional co-precipitation, with the gel of zinc sulfide which has led in the end even to the formation of an independent thallium mineral, in the course of the diagenesis. The relative abundance of the micro-inclusions of thallium minerals in the sulfides of the deposit is suggested, in our view, by the high thallium content of the original ore, as well as of the concentrates from the ore-dressing plant, in comparison with the thallium content of the pure minerals here examined (Table 1). Since the iron bisulfides in which the concentrations of thallium attain their maxima are not abundant among the ore minerals of the Kvaisa (about 0.1% iron both in lead and in zinc concentrates), the relatively high content of thallium in the ores and in the concentrates hardly can be attributed to iron.

As shown in the diagram, the content of thallium increases parallel with an increasing content of either arsenic or of antimony, but never parallel to both of them. The contents of arsenic and antimony vary antipathetically, as if they were competing with one other for a place in the crystal lattice of galena.

Such distribution of the elements indicates the possibility of a compensating isomorphism between lead ion couples and the $Tl^+ - As^{3+}$ and $Tl^+ - Sb^{3+}$ couples, by the reaction $2Pb^{2+} \rightarrow Tl^+As^{3+}$ or $2Pb^{2+} \rightarrow Tl^+Sb^{3+}$. There is no bismuth in the galenas of the Verkhnyaya Kvaisa.

As to the presence of thallium in marcasites—our data are insufficient for an opinion regarding its forms, because only three samples of marcasite were examined. We may only report a thallium-arsenic paragenesis in the marcasites.

The behavior of thallium in the oxidized zone, in the upper horizons of the deposit, which were subjected to an intensive oxidation and water-working, is very interesting. Thallium is absent in these oxidized ores and its absence is easily explainable by the high solubility of its sulfates and carbonates which must have been carried away by the mine waters outside the boundaries of the deposit.

In conclusion, we must call attention once again to the existence of independent thallium minerals in the deposit, a fact not only of fundamental but also of practical significance.

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EDITOR'S NOTE:

Mention is made by the authors of the summary work by M. J. Fisher, "Minor elements in some sulfide minerals," *Econ. Geol. Anniversary Vol.*, Pt. 2, pp. 970-1024, which deals not only with the problem of distribution of thallium among co-existing sulfides but also with other minor elements in similar environments.

E. W. H.

GEOCHEMISTRY OF THALLIUM IN ALKALIC ROCKS, WITH MT. SANDYK MASSIF (NORTHERN KIRGIZIYA) AS AN EXAMPLE

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Abstract

The distribution of Tl in various alkaline rocks of the Sandyk massif (monzonites, alkali earth syenites, alkaline and nepheline syenites) and its bond to K have been studied. The average value of the K/Tl ratio for the massif is 3.63×10^4 . The petrogenetic significance of deviations from this value in the case of vein rocks is shown. It has been found that all the Tl of the rock is distributed among orthoclase and biotite; the preferred Tl accumulation in biotites is explained from crystal chemical viewpoints. The very close dependence of the Tl behavior on that of K is determined during the process of rock crystallization itself. In the general evolutionary process of the alkaline magma, leading to the formation of successive differentiates, this dependence shows a number of deviations.

A close relationship of thallium with the alkali metals was reported in the first review of the geochemistry of thallium by V. I. Vernadskii, in 1909, with the supposition that: "... in the deep layers of the lithosphere. ... thallium is completely dispersed in the form of a minute isomorphous admixture" [1, p. 427]. These hypotheses were confirmed by later studies dealing with determinations of thallium in igneous rocks and in natural silicates, with certain elaborations, by V. M. Goldschmidt, L. H. Ahrens, I. P. Novokhatskii and S. K. Kalinin, D. M. Shaw, and other investigators. In addition to these primarily statistical data, a report by L. V. Tauson and N. N. Buzaev [2] appeared recently in which there is a detailed analysis of the distribution of thallium accompanying the formation of the intricate granitoid complex of the Susamyr batholith. The authors suggest a genetic correlation between certain granites of the batholith by means of certain relationships established. In the meanwhile, we still know only too little about the behavior of Tl in alkaline-magmatic processes, especially regarding data for alkaline rocks of different types.

For example, the following analyses (6 samples) of rocks from different sources are reported by D. M. Shaw, in the most complete account thus far of the geochemistry of thallium [3]:

- | | |
|------------------------|------------|
| 1. Monzonite; Colorado | 1.7 ppm Tl |
| 2. Syenite; Ontario | 1.1 ppm Tl |
| 3. Syenite; Ontario | 1.3 ppm Tl |

4. Phonolite; Colorado	7.2 ppm Tl
5. Nepheline syenite; Ontario	2.2 ppm Tl
6. Ijolite; Finland	1.4 ppm Tl

the averages for syenite and monzonite, 1.4 ppm Tl (averages for first three samples), and 3.6 ppm for nepheline rocks (averages for first three samples) reported by this author must be taken merely order-of-magnitude values, because of the obvious insufficiency of data. The need of augmenting our fund of knowledge of Tl in alkalics is self-evident. There is much more interest in the behavior of Tl in alkalic rocks within one single genetic series in which there is a definite sequence in the magmatic differentiates. The present study throws some light on previously posed problems, using the Mt. Sandyk alkalic Massif as an example.

BRIEF ACCOUNT OF COMPOSITION AND STRUCTURE OF MT. SANDYK ALKALIC MASSIF

The alkalic Mt. Sandyk massif is situated in the high-mountain area of the Dzhungol-Tau Range which belongs to the northern arc system of the Tyan-Shan in Northern Kirgiziya. The geologic history of the massif shows typical Caledonide features of the Northern Tyan-Shan. The massif is associated with the Hartz fissuring zone of the ancient crust which, according to N. M. Sinitsyn [4], follows the junctures between the Caledonides proper and areas of development of the Middle Paleozoic epi-Caledonide structures.

The host rocks of the Mt. Sandyk massif are chiefly different varieties of granite of the Susamyr batholith, of Caledonian age, and, to a certain extent, Lower Silurian sandstone-shale formations and meta-sedimentary facies of the undifferentiated Lower Paleozoic. The alkalic massif forms clearly defined intrusive contacts with its host rocks. The massif was formed during the Variscan tectono-magmatic epoch. However, its exact age has not been ascertained.

The original data on composition and structure of the Mt. Sandyk massif were provided by the geologic survey studies of K. D. Pomazunov of the Kirgiz Geologic Administration. In 1953-1956* studies by the author of the present report indicated a far more complex structure of the massif than was previously believed. These studies discovered nepheline syenites of the miascite type among the components of the massif together with their pseudoleucitic varieties.

The Mt. Sandyk alkaline massif is a complexly differentiated two-stage intrusion of hypabyssal emplacement. The visible outcrops area of the intrusive body constitutes about 70 square kilometers. The rocks composing the intrusion belong to the syenite clan and their age to the time of their formation are very close to each other.

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Among these rocks, the following characteristic types are distinguished:

Phase I: (a) alkalic gabbroids (monzonites, monzonite-essexites, monzonite-shonkinites); (b) alkaline-earth syenites; (c) facies of leucocratic alkaline-earth syenites.

Phase II: (d) hornblende alkalic syenites; (e) nepheline syenites.

Approximate areas occupied by these rocks are reported in Table 4.

There is a definite zoning in the massif structure. Thus the rocks of Phase I compose the periphery and the top parts of the intrusive body, whereas the rocks of Phase II are at depth and in the core. At the same time, in Phase I types, the earliest rocks (the alkalic gabbroids) generally occupy the margins and apexes, whereas the leucocratic syenites occupy the interior where they often form the boundaries between Phase I and Phase II. Variations from this lithologic zonation are due to the manner in which the intrusion formed, i.e., in an unstable tectonic environment, as indicated by the trachytoid fabric common in the rock structures.

Table 1. Distribution of Thallium among Minerals in Some Principal Alkalic Rock Types of Mt. Sandyk Massif

Mineral	Wt. % of mineral in rock	ppm Tl in Mineral	Tl in mineral relative to total Tl in rock	
			ppm	wt. % (total Tl = 100%)
Sample 265. Porphyry-like alkaline-earth syenite, Phase I (1.1 ppm Tl)				
Orthoclase	68.1	1.2	0.82	74.5
Plagioclase	7.9	n.d.*	--	--
Pyroxene	15.0	n.d.	--	--
Biotite	7.1	3.2	0.23	20.9
Sum	98.1	--	1.05	95.4
Sample 1147. Hornblende alkalic syenite, Phase II (2.2 ppm Tl)				
Orthoclase-perthite	87.9	2.5	2.19	99.5
Plagioclase	0.81	n.d.	--	--
Hornblende	9.9	0.7	0.07	3.2
Biotite	0.22	7.6	0.01	0.4
Sum	98.83	--	2.27	103.1
Sample 268. Nepheline syenite, Phase II (2.7 ppm Tl)				
Orthoclase	75.0	3.4	2.55	94.4
Nepheline	15.6	n.d.	--	--
Augite	1.3	n.d.	--	--
Biotite	4.3	5.3	0.23	8.5
Sum	96.2	--	2.78	102.9

*n.d. = not determined

Table 2. Thallium in Rock Types of Mt. Sandyk Alkalic Massif (ppm)

Sample No.	Rock	Tl, ppm	% K*	K/Tl ratio as %x10 ⁴
Alkalic Gabbroids, Intrusive Phase I				
271	Monzonite-essexite, olivine rich	1.0	--	--
1055	Monzonite-essexite	1.2	4.54	3.78
1411	Monzonite-shonkinite	1.3	--	--
	Average	1.16	--	--
Ic	Composite of 6 Monzonites, incl. Items 1-3	1.1	4.30	3.90
Porphyritic Alkaline-earth Syenites (pyroxene-biotite), Intrusive Phase I				
1174	Monzonite-like syenite	1.2	--	--
1157	Monzonite-like syenite	1.0	--	--
265	Monzonite-like syenite	1.1	5.10	4.63
1171a	Alkaline-earth syenite	1.7	4.67	2.74
1052	Alkaline-earth syenite	1.0	--	--
	Average	1.2	--	--
IIc	Composite of 12 Syenites, incl. Items 5-9	1.6	5.05	3.15
Series of Leucocratic Alkaline-earth Syenites, Intrusive Phase I				
1060	Leucocratic syenite	1.8	--	--
1180	Leucocratic syenite	2.0	--	--
1155	Leucocratic syenite	1.3	--	--
808	Leucocratic syenite	1.8	5.55	3.08
254b	Leucocratic syenite with epimagmatic hornblende	2.0	7.88	3.94
1057	Leucocratic syenite, appreciably altered	2.3	--	--
	Average	1.9	--	--
IIIc	Composite of 11 Syenites, incl. Items 11-16	2.0	5.75	2.87
Hornblende Alkali Syenites, Intrusive Phase II				
1048	Melanocratic syenite	1.6	--	--
1147	Medium-grained syenite	2.2	--	--
817	Coarse-grained syenite	1.8	8.35	4.64
XIV	Fine-grained syenite with melanite	2.3	8.64	3.76
269	Leucocratic syenite	2.2	8.22	3.73
1050b	Leucocratic syenite	1.9	--	--
	Average	2.0	--	--
IVc	Composite of 11 Syenites, incl. Items 18-23	2.0	7.06	3.53

Table 2. (continued)

Item No.	Sample No.	Rock	Tl, ppm	% K*	K/Tl ratio as %x10 ³
(e) Nepheline Syenites, Intrusive Phase II					
25	268	Biotite syenite	2.7	10.20	3.78
26	813	Biotite syenite	3.0	--	--
27	1049a	Biotite syenite with sodalite	4.4	9.50	2.15
28	1069	Pseudoleucitic biotite hornblende	2.9	10.70	3.69
29	1065	Biotite-barkevikite-pyroxene	1.5	--	--
		Average	2.9	---	--
30	Vc	Composite of 11 Syenites, incl. Items 25-29	3.7	8.00	2.16
(f) Vein Rocks Related Spatially to Rocks of Intrusive Phase I, Vein Series					
31	728	Monzonite(shonkinite)-porphyry with inclusions of pyroxene	1.0	3.5	3.5
32	723	Fine-grained monzonite-shonkinite	1.4	--	--
33	1073	Syenite-porphyry with inclusions of K-Na feldspar and epileucite	1.0	6.10	6.1
34	1054	Irregularly-grained leucosyenite	1.4	--	--
35	1155	Aplitic syenite with quartz	1.6	--	--
36	1050	Quartz syenite-aplite	2.2	7.33	3.33
(g) Vein Rocks Related Spatially to Rocks of Intrusive Phase II, Vein Series					
37	1071b	Medium-grained leuco-syenite with aegirine and quartz	2.1	9.55	4.54
38	1152c	Medium-grained leuco-syenite with alkali amphibole and quartz	2.5	--	--
39	1192	Leuco-syenite with hackmanite and nepheline	3.0	--	--
40	268a	Sodalitic bostonite with nepheline, fluorite, and admixture of biotite	5.0	5.30	1.06

*Potassium was determined at the V. I. Vernadskii Memorial Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR, by V. I. Lebedev (flame photometry) and by L. A. Pevtsova (chemically, in samples 1055, 265, 808, 254b, 269, 268, 1050).

The rocks have the following mineralogical characteristics:

1. K-Na feldspar (orthoclase and anorthoclase) is markedly preponderant in all syenitic rocks (with the exception of certain alkalic gabbroids), which is an indication of a predominantly potassic magma. The K content of the rocks is reported in Table 2.

2. Syenites of Phase II, in comparison with syenites of Phase I, are relatively enriched in certain volatile constituents: F, Cl, H₂O (indicated by the presence of fluorite, sodalite, zeolites, and hornblende, as primary minerals).

3. Monoclinic calcium pyroxene (augite to salite), biotite, and

ary hornblende (in places, resembling ferrohastingsite or barke-) are common dark mineral accessories in the intrusive rocks.

Post-magmatic alterations or metasomatic transformations are characteristic of the massif.

Structural interrelations of the rock-forming minerals indicate that orthoclase was formed later than the feldspars and pyroxenes. Orthoclase is prismatic, as a rule, forming inclusions in porphyroid varieties of the rock, and may be regarded here as an early mineral. The veins are the alkalic gabbroids in which monzonitic structures are developed by K-Na feldspars. Nepheline of nepheline syenites generally fills the spaces between the orthoclase minerals and belongs to a late crystallization phase.

The alkalic magma of the intrusion was subjected to drastic differentiation into a mafic alkaline-earth phase (the early and upper zone) and a leucocratic alkalic phase (the late and deeper zone).

The Vein Series of the intrusion are weakly expressed, but are represented by highly varied syenitic types which seem to reflect the various rock types of the massif in their composition. Thus augite-syenite and augite-monzonite (shonkinite) porphyries, syenite-porphyrates, various leuco-syenites, and syenite-aplites are distinguishable in the Vein Series. These representatives of the Vein Series are generally found in rocks of Phase 1. Among Phase II rocks we find chiefly fluorite-free and quartz-leucosyenites and bostonites which are commonly enriched in fluorite, nepheline, and sodalite. These are the characteristic minerals of Phase II (Table 2).

Table 3. Average Thallium in Rocks of Principal Stages of Differentiation of the Intrusion

Stage	Tl, ppm
Alkalic rocks of Phase I (alkali gabbroids, alkaline-earth syenites, facies of leucocratic syenites)*	1.7
Alkalic rocks of Phase II (hornblende-alkalic syenites and nepheline syenites)*	2.5
Vein rocks related spatially to rocks of Phase I	1.4
Vein rocks related spatially to rocks of Phase II	3.1

*Thallium averages are calculated on the basis of the composite averages (Table 2), taking into account the relative abundance of the rocks.

The Vein Series sequence is difficult to establish because vein interrelations are absent. However, a certain spatial association between the various phases and the vein rocks of this or that type allows us to propose some definite genetic relationships between the vein rocks and corresponding phases of the intrusion.

Table 4. Calculated Thallium Averages for the Mt. Sandyk Intrusion

Rock type	Visible outcrop area		Average Tl in rock types,* ppm	
	km ²	% area	Arithm. averages	Composites
(a) Alkalic gabbroids	8	11.4	0.13 (3 samples)	0.13 (6 samples)
(b) Alkaline-earth syenites	25	35.7	0.43 (5 samples)	0.57 (12 samples)
(c) Leucocratic syenite facies	22	31.5	0.60 (5 samples)	0.63 (11 samples)
(d) Hornblende alkalic syenites	10.5	15.0	0.30 (6 samples)	0.30 (11 samples)
(e) Nepheline syenites	4.5	6.4	0.18 (5 samples)	0.23 (11 samples)
Sum	70	100.0	1.6	1.9

*Calculated from data in Table 2.

Methods

In the present study 44 rock and 7 mineral samples isolated from the rocks were examined. The small amounts of Tl were determined colorimetrically, by the method proposed by N. T. Voskresenskaya [5]. Reliability of the determination was ± 15 to 20%, with a sensitivity of 0.03 micrograms per milliliter. The colorimetry was visual by means of a scale of standards.

Samples that were selected for the analysis were free from secondary alteration or were affected by them only to an insignificant degree; the selection was monitored using a microscope.

In addition to individual samples from cores, we also analyzed composited samples representative of intrusive facies of each differentiation phase. The composites were prepared from samples taken for separate analyses and from equal quantities of samples of analogous rock types, which were not separately analyzed. Suitability of such procedures is discussed below.

The isolation of rock minerals from the fine fraction (< 1 mm) was done under a binocular lens of the MBS-2 Type. The quantitative mineralogic estimations for three samples (Table 1) were made in large thin sections using L. V. Dmitriev's method [6].

DISTRIBUTION OF THALLIUM DURING CRYSTALLIZATION OF THE MT. SANDYK ALKALIC INTRUSIVE

It has been shown in earlier studies that Tl accumulates chiefly in potassium minerals of igneous rocks, in micas and in K-Na feldspars

[2, 3, 7, 8, 9], where it replaces K or Rb isomorphously. For this reason, in the case of the three typical representatives of the alkalic rocks of the massif (Table 1), biotite and orthoclase were analyzed, in one instance, on the supposition that these minerals may serve to describe the behavior of Tl during crystallization of the corresponding magma into the rock. Hornblende was analyzed only in the case of sample 1147—the only dark mineral, for all practical purposes.

As shown in Table 1, all or almost all of the thallium, in the three samples, is distributed between orthoclase (74 to 99%) and biotite (8.5 to 10%). There remains only an insignificant fraction of the total thallium of rock to be shared by the other rock-forming minerals: pyroxene, plagioclase, and nepheline. This conclusion is validated by a satisfactory agreement between the calculated and the determined total thallium in the rock. The differences are within the limits of analytical errors.

Our results show that Tl follows K, replacing it isomorphously (Tl^+ , $R = 1.49 \text{ \AA} \rightarrow \text{K}^+$, $R = 1.33 \text{ \AA}$), in the crystallization of the alkalic rocks here discussed. J. Otteman* and D. M. Shaw report the possibility of finding thallium in Ca-silicates (R (of calcium) = 1.06 \AA); for example, in hornblende and in calcic plagioclase.

This latter type of the replacement is probably very restricted because in our case the bulk of Tl is monovalent. The up-take of Tl in sample 1147 hornblende, sample 1147 (0.7 ppm Tl) is probably due to an substitution of K, since the hornblende contains about 1 to 3% K, by semi-quantitative spectrographic analysis. There is no detectable accumulation of thallium in sample 265 (Table 1) either in the calcium plagioclase (an₄₃) or in the pyroxene (salite-augite). $\text{Tl}^+ - \text{Ca}^{2+}$ and $\text{Tl}^+ - \text{Na}^+$ (1.98 Å) isomorphism is inhibited by the excessive differences between their ionic radii.

In every case our findings indicate Tl concentration in biotites is higher than in orthoclases. The same was reported by many other investigators [2, 3, 8, 9]. It is believed that this phenomenon is controlled upon a freer position of K in biotite structures than in K-Na plagioclase [2].

Indeed, the coordination number of 12 is characteristic for the large K in [10]. The coordination of K is the same in biotite, whereas in orthoclase its coordination is 9 at best [11, 12, 13]. Moreover, according to N. V. Belov, K is situated in the weakly bonded portions of the crystal structure (along cleavage planes). Here, the large K-octahedra connect the "3-packet" layers consisting of small tetrahedra and octahedra. Although the Tl^+ ion is geometrically larger than K^+ it nevertheless may easily be accommodated in this weakly bonded layer displaced by K ions. This is not the case in K-Na feldspars. According to N. V. Belov [13], in orthoclase structures, K^+ is distributed between

* Not referenced; presumably *Zeit. angew. Min.*, v. 3, p. 142 (1940).

tightly bonded rings consisting of (Si, Al) tetrahedra joined into strong chains. Tl^+ , the larger ion, while replacing K^+ , would cause a greater deformation of the structure. Also, the orthoclase structure is not a densely packed one and its specific volume is larger than it is in other silicates [14]. For these reasons, structural deformations are especially unfavorable for orthoclase.

Consequently, although the replacement of K^+ by Tl^+ does take place in orthoclase, it takes place with greater difficulty than in the case of biotite. Apparently the restrictions limiting the replacement of K^+ by Tl^+ in orthoclase, an earlier mineral, contribute to the accumulation of Tl in biotite, a later mineral, in the rock types discussed here. It is not difficult to see in Table 1 that, the higher the total thallium in the rock, the higher is its concentration in orthoclase and biotite of the same rock. True, the high Tl content in biotite in sample 1147 (7.6 ppm Tl) is evidently related to the very low content of biotite itself (0.22% biotite in the rock). The enrichment of Tl in the late magmatic accumulates accounts for this high degree of scavenging of Tl by what little biotite existed.

The following fact deserves our attention. The Tl content of the three samples here studied increases from the earliest (sample 265) to the latest one (sample 268). This result is discussed in greater detail below. We may merely remark here that the cause of such accumulation of Tl may not be entirely dependent on the crystallization sequence of the rock-forming minerals and on the distribution of thallium between these minerals in this process. Indeed, if there were any excess of Tl in the original rock and if this excess had been transferred into the late-stage solutions in the course of the crystallization, this excess would have been captured entirely by the biotite of the original early rock. The biotite in this early rock (sample 265) is one of the youngest minerals and yet its Tl content is the lowest of the three. Analogous examples may lead us perhaps to certain definite modifications of current ideas regarding direct relationship and dependence of the sequence of formation of rocks and crystallization of magma as such.

BEHAVIOR OF THALLIUM IN DIFFERENTIATION OF THE ALKALIC INTRUSION OF MT. SANDYK

Table 2 lists the Tl content in the alkalic rock types of the intrusion in the sequence of their formation and also includes the most typical representatives of the Vein Series. The data in table 2 indicate a gradual, progressive 2- to 3-fold increase in the Tl content from the earliest rocks, the alkalic gabbroids of Phase 1 (1.1 ppm Tl) to the later differentiates of the intrusion. One may easily see that this principal trend in the behavior of thallium is in harmony with the progressively increasing potassium content of the rocks. Excluding the Vein Series the relationship of Tl and K in the intrusive rocks is indicated by the relatively small range of fluctuation of the K/Tl ratio (4.64×10^4 to

$\times 10^4$) with an average of 3.63×10^4 as indicated by the analyses of 2. Fluctuations of the ratio within the limits of the range are irregular.

We should observe here that our results for the K/Tl ratio lie between the averages of 5.69×10^4 and 1.09×10^4 , for gabbro plus basalt and granite, respectively as given by D. M. Shaw [3]. Thus the acidic rocks of Mt. Sandyk examined are somewhat impoverished, with respect to Tl versus K, relative to granites, but are somewhat enriched, with respect to Tl, relative to gabbro and basalt.

Thallium averages are compared in different rock types (intrusive types "a", "b", etc.), as arithmetical means for each type, with respect to the composites, the two values show in general satisfactory agreement. We cannot draw the same conclusion for K because the number of determinations of this element is insufficient for such comparisons. However, the average K/Tl ratios in the composites (3.12×10^4) are sufficiently close to the averages based on analyses of individual samples. In such a way, we are able to ascertain general relationships in the behavior of a rare element (thallium, in our case) during emplacement of the intrusion, on the basis of composite samples consisting of genetically and materially similar phases of the intrusion. At the same time, it is essential to also examine the individual samples, because possibly certain local features or anomalies in the geochemical behavior of the element in question may be discovered which are nonetheless important. For example, if we examine the scatter of thallium concentrations in the rocks studied, we observe that thallium "highs" do not always go together with potassium "highs" in a given sample. Such divergencies may be ascribed, in part, to shortcomings of the analytical methods. However, they are sufficiently conspicuous in a number of cases to compel us to look for other explanations. Thus, in an alkaline-earth syenite 1171a, of low potassium content (4.67%), there is 1.7 ppm Tl, i.e. nearly twice as much Tl as in a similar sample 265 which, moreover, is somewhat higher in K (5.47%). Some nepheline syenites contain both too high and too low thallium, 4.4 ppm and 1.5 ppm Tl respectively, while their K content is about the same. Representatives of the Vein Series of the intrusion show even greater abnormalities. Such anomalous behavior of thallium, together with its general geochemical relationship with potassium in the evolution of an alkali intrusion may be explained, from our viewpoint by the following considerations:

First, such an anomalous behavior may result from an originally irregular distribution of Tl in the alkalic magma at the time of its origin. This original irregularity may be continued somehow through the further development of the magma chamber and may be imposed accordingly on the geochemical behavior of thallium.

Second, thallium "highs" may be explained by the mobilizing influence of other elements whose local accumulations depend on such effects. Specifically, Cl, F, H_2O —the volatile constituents of the magma—function as mobilizers. As previously noted, such elements

accumulate in the terminal stages of magmatic differentiation, in Phase II of the intrusion, as well as in some of the vein rocks. It has been noted that the highest amounts of Tl are found in rocks which contain sodalite 4.4 ppm, 3.0 ppm, 5.0 ppm Tl, in samples 1049a, 1192, and 268a respectively. It is possible, in this case, that Cl is conducive to an accumulation of Tl in the melt because it forms strongly associated monochlorides of Tl [15]. The monochlorides become dissociated during magmatic crystallization, whereupon Tl follows K, in its passage into potassium minerals.

Third, the anomalous behavior of Tl may be due to the "inheritance" factor, in the evolution of the magma chamber, as may be seen in the Vein Series of the intrusion. Indeed, it is not possible for us to establish any definite relationship between Tl and K for the vein rocks, as reported in Table 2. The very wide range of variation in the K/Tl ratio, from 1.06×10^4 to 6.1×10^4 , also points in this direction. However, an interesting relationship of a different kind is conspicuous here. It turns out that Tl is impoverished in rocks which are related spacially to the rocks of Phase I with respect to rocks related spacially to the alkalic rocks of Phase II. This coincidence may be illustrated by the thallium averages shown in Table 3.

One may suppose that a relationship of this sort is not accidental but is an expression of a genetic relationship between the vein derivatives and the corresponding phases of the intrusion. We cannot exclude the possibility that the "inherited" behavior of Tl or other trace elements in the formation of a complex plutonic alkalic body may serve as an example of an auxiliary method in ascertaining genetic relationships of vein rocks in multi-phase plutonic bodies of different compositions. The calculated arithmetic average content of Tl of the intrusion, taking into account the areas occupied by different rocks (Table 4), indicates rather too low a value (1.6 ppm Tl) versus the value based on analyses of the composites (1.9 ppm Tl).

The scattering of the thallium values in samples within a facies leads us to a greater reliance on thallium averages in composited samples, inasmuch as the composites represent about twice as many samples as we examined separately. Accordingly, 1.9 ppm Tl is taken here as the average thallium content of the intrusion. This figure is very close to the A. P. Vinogradov's thallium average for igneous rocks [16] 1.7 ppm Tl (2 parts of felsic rocks plus 1 part of mafic rocks) and is somewhat higher than D. M. Shaw's figure [3] for thallium in the earth's crust: 1.3 ppm Tl.

Our data on the relative abundance of thallium in the alkalic rocks of the Mt. Sandyk massif are by no means all-inclusive for such types of igneous rocks, even though we did encounter nearly equivalent concentrations of thallium in abyssal alkalic rocks from Ontario and Colorado according to Shaw [3]. Thus four typical samples of alkalic rocks from the Khibina massif show extremely low thallium content:

1. Massive khibinite	0.6 ppm Tl
2. Trachytoid khibinite (eudialite)	0.6 ppm Tl
3. Urtite - ijolite	0.7 ppm Tl
4. Massive foyaite	0.8 ppm Tl
Average	0.7 ppm Tl

the same time, Shaw reports 1.4 ppm Tl in the ijolite from Fin-
The cause of such an impoverishment of thallium in the Khibina
is related apparently to the originally low thallium contents of
primary alkalic magma of the Khibina plutonic body. A more def-
view on the subject may be afforded, it appears, by a more de-
study of the problem.

CONCLUSIONS

A geochemical relationship between Tl and K becomes manifest
magmatic differentiation and crystallization of the alkali magma
Mt. Sandyk intrusion. This relationship clearly exists during
crystallization process when all of the Tl is distributed between the
silicate minerals (orthoclase and biotite). A series of concentration
variations develop along with a general tendency toward accumulation
of thallium in the later potassium-enriched derivatives, in the course
of differentiation of the alkalic magma. Such anomalies are due ap-
parently to several causes which deserve further investigation.

The following thallium averages are observed among the intru-
sion series, from the earliest to the latest facies: 1.1 ppm Tl in
gabbroids; 1.6 ppm in alkaline-earth syenites; 2.0 ppm in leuco-
syenites; 2.0 ppm in hornblende-alkali syenites; 3.7 ppm in
alkaline syenites of the miaskite type. The average for the intrusion
is 2.0 ppm Tl, with an average K/Tl ratio of 3.63×10^4 .

An additional genetic indication as to the position of the Vein
in the intrusion emplacement sequence is provided by the "in-
crease" of thallium concentrations in the vein rocks which are re-
lated spatially to the intrusion phases and in the relative abundance of
thallium in these phases.

The preferential up-take by biotite structures, as against ortho-
cline structures, is explainable by the different crystal-chemical posi-
tion of potassium in these structures as well as by the structures
themselves wherein Tl substitutes for K. It should be emphasized that
these results suggest the need of comparisons between a largest possible
number of average samples representing genetically related rocks in
order to ascertain their thallium averages.

In conclusion, the author takes this opportunity to express his thanks
to V. Tauson for his sustained interest and advice in the present
work, to N. T. Voskresenskaya for her consultation regarding technique
of thallium determination, to V. I. Lebedev and L. A. Pevtsova for their
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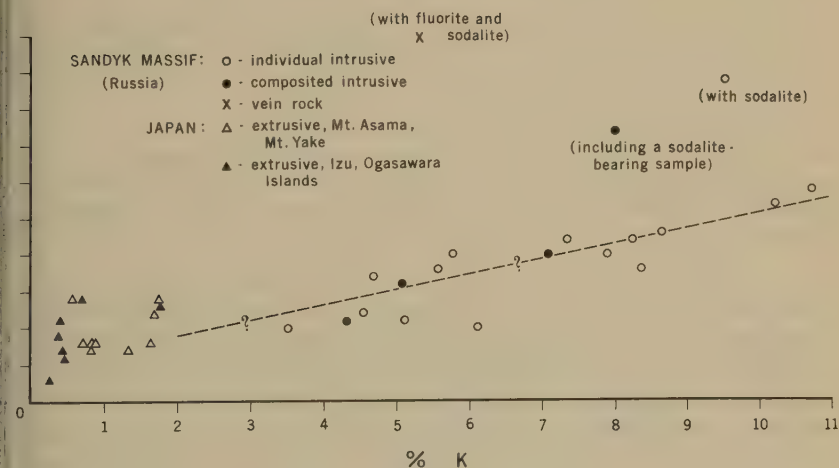
for their kindness in placing the samples from the Khibiny alkaline massifs at the author's disposal.

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AUTHOR'S NOTE:

Good examples of locally operative geologic processes superposed on generally operative processes are worth elaboration. In the above diagram, the overall increase in thallium concentration with stage of magmatic differentiation is recognized. However, the thallium content anomalies are attributed to locally operative processes of geochemical significance. The abnormally high thallium values in sodalite bearing rocks and the highest content in a sodalitic bostonite with free fluorite are evidence strengthening Zlobin's ideas of localized halogen transport of thallium with isomorphous substitution of Tl for K at any stage during the magmatic crystallization process. Thus anomalies in Tl versus K scatter diagram would seem reasonable. Such scatter appears in Japanese extrusives (Ishimori and Takashima, 1955, p. 65-72) and is plotted together with the Russian data below.



Thallium and potassium correlation of Northern Kirgizia intrusive alkalic rocks (this paper) and Japanese extrusive volcanic rocks

REFERENCE

Ishimori, T., and Takashima, Y., 1955, Thallium content of Japanese igneous rocks: Dept. Chem., Faculty of Sci., Kyushu Univ., Mem., Ser. C (Chem.), v. 2, No. 2, p. 65 - 74 (in English).

J. G.

RELATIONSHIP BETWEEN COMPOSITION OF RARE EARTHS AND COMPOSITION AND STRUCTURES OF MINERALS

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Abstract

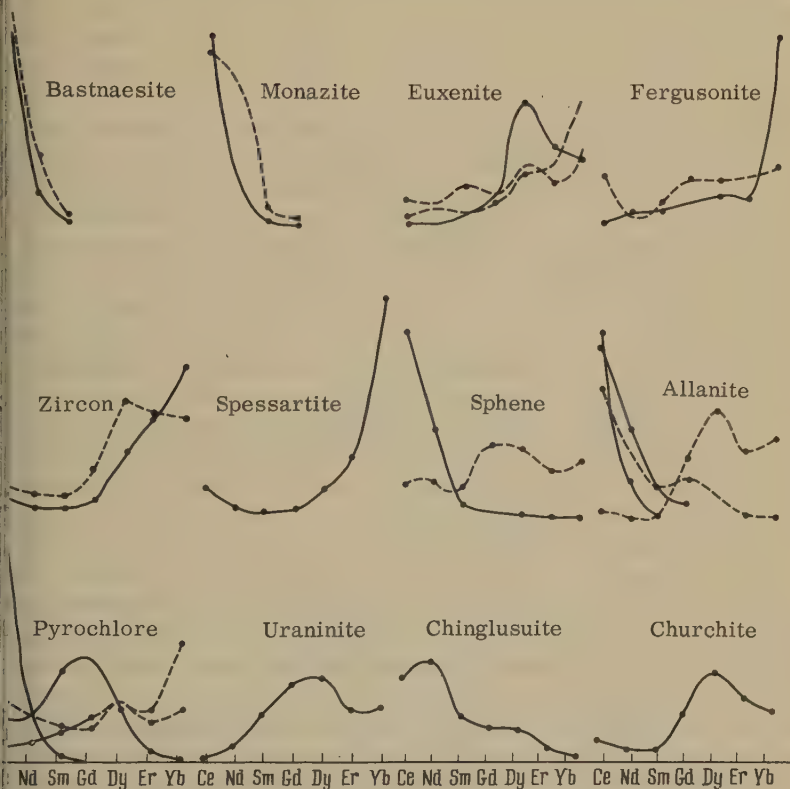
It has been shown that, according to the isomorphism capacity, complex and selective rare-earth minerals (cerium, gadolinium and yttrium minerals) are isolated. The selectivity degree of minerals is determined according to the amplitude of composition change of TR and of their ionic radius. In minerals not of the rare-earth group the composition of rare earths is determined by their closeness of the ionic radius to the element being replaced. Thus, the minerals of Sr, Ba, K are usually selective ceric; minerals of Zr, Sc, Fe—selective yttrium; of Ca—complex minerals.

The composition of TR may serve for diagnostic purposes and for identification of selective minerals. In selective minerals the composition of TR is determined according to the crystallochemical structure of minerals which limit the isomorphism capacity, in complex minerals—according to the medium, to the composition of TR in the initial melt or solution.

Experimental findings and a discussion of relationships affecting composition of the rare earths in minerals (and chemical sediments), in general, regardless of their crystallochemical characteristics, were presented in a preceding report [1]. However, as has been already shown [2], there are very appreciable differences between minerals in regard to the range of variations of their rare-earth compositions. Even if the role of crystallochemical structures is denied in the paper by Murata et al. [3], serious restrictions, due to inner structures of minerals, are often imposed on variations in the composition of the rare earths in minerals.

Many of the rare-earth minerals have a limited capacity for isomorphism. Such is the case with monazite, loparite, and others. These minerals have one and the same maximum, in all known instances, specifically, the cerium maximum. At the same time, the rare earths of pyrochlore, in different samples from different sources, have their maxima practically at all of the even-numbered lanthanoids: Sm, Gd, Dy, Yb (see sketch).

Minerals whose isomorphism is restricted and whose rare earths are not able to influence position of the maximum may be termed "selective"; minerals whose isomorphism is effective within a wide range and whose rare earths are capable of influencing position of the



Variations in composition of even rare earths in different minerals.

num may be termed "complex". Cerium, gadolinium, and yttrium selective minerals may be distinguished by the position of the maximum. Cerium selective minerals are especially abundant in their distribution (monazite, bastnaesite, loparite, etc.), and so are the yttrium selective minerals (euxenite, xenotime, etc.). Selective gadolinium minerals are far more rarely and are not as definitely identified.

We need the dividing line between the selective and the complex minerals is drawn essentially on the basis of statistical data. For example, more than 100 specimens of monazite were examined and all of them proved to be of the cerium type. We have confidence, therefore, that frequent studies of monazite will not result in discoveries of the presence of other rare earths. At the same time, in the case of samarskite—a supposedly selective gadolinium mineral, only five specimens were examined. Four of them proved to be of the gadolinium type—and this fact is the basis of the present hypothesis. There is no guarantee,

however, that other specimens of this mineral may not show some other maxima, especially since one of the samarskite specimens already proved to be higher in Dy than in Gd. In this particular case, since the range of variation in composition the rare earths is relatively narrow, and since the composition curve is of the simple type, we shall continue to classify samarskite as a selective mineral, although the extent of its selectivity is not as great as it is in the selective cerium minerals. It should be more appropriate to call samarskite a selective mineral with the centered maximum, since it contains also large quantities of Sm, Gd, and Dy—the elements occupying the center of the lanthanide series. A lecture group of minerals is known only by a single analysis of their rare earths (florencite, nordite, hellandite), and statistical methods cannot be applied to them, for that reason, in determining the extent of their selectivity. The difficulties are increased further by the fact that several minerals are found only in some one particular deposit, out of the whole world, and that, consequently, the chances of discovery of variations in their rare-earth composition are very small. For example, chinglusuite is found only in one unique deposit. There is a basis for regarding this mineral as the first one of the selective neodymium type, since a small neodymium peak was discovered on its detailed analysis—the only analysis at that.

One may maintain, nevertheless, that florencite and nordite are selective cerium minerals, because of the known and markedly cerium-selective composition of their rare earths, because their rare earths are associated with strontium and barium, and because of the high coordination number of the rare earths present in their crystal structures. Indeed, it has been shown [2] that rare earths in minerals of the selective type have the extreme possible coordination numbers (with the maxima of 10 to 12 for cerium and with the minima of 6 to 8 for yttrium), whereas the coordination numbers are intermediate (7 to 9) in the case of rare earths in minerals of the complex type. This regular relationship holds in the ordinary environments in which there is a deficiency of the central members of the rare-earth series (Sm, Gd). In uniquely exceptional environments of the formation of minerals, selective with respect to these two members of the rare earths, the coordination numbers will be probably within the intermediate range. Britholite and allanite are among the most highly complex rare-earth minerals. Their high complexity may be due to two different coordinations of Ca and of the rare earths (7 and 8 in allanite; 7 and 9 in britholite). The relationship between the rare-earth composition and the coordination numbers enables us not only to predict, on the basis of the coordination number, whether the mineral belongs to the selective or to the complex type but also to solve a converse problem, namely to predict the coordination number from the rare-earth composition. This is applicable not only to the rare earths but also for other isomorphous ionic groups (Ca-Sr; Ti-Zr; etc.).

In the case of so-called rare-earth minerals containing only small quantities of the rare earths, the role of structure may be exemplified

calcium minerals. Indeed the coordination of Ca in perovskite is 12, as calcium is replaceable only by the cerium rare earths. However, both cerium and yttrium rare earths are present in sphene where the coordination of Ca is 7. Yttrium rare earths are probably more characteristic of calcite, with its 6-coordinated Ca.

Not only the mineral structure and the coordination number of the rare earths contained in the mineral, but also the individual characteristics of the mineral exert a substantial influence on the rare earth composition of the minerals with but minor rare earths (especially of the Mn-free minerals).

Thus, in garnets, $(\text{Ca}, \text{Mg}, \text{Mn}, \text{Fe}^{2+})_3(\text{Al}, \text{Fe}^{3+})_2\text{Si}_3\text{O}_{12}$, the ions of Ca, Mg, Fe²⁺ and their rare-earth substitutes have one and the same coordination of 8. However, the rare-earth composition is not the same in different garnets.

Characteristic in spessartite, $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, the rare earths are of the selective yttrium type, with the ytterbium maximum among the lanthanides, whereas in andradite, $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, the rare earths are of the complex type and have a small cerium maximum. It is evident that Mn in spessartite is more readily replaced not by the cerium but by the yttrium rare earths whose ionic radii are closest to the ionic radius of Mn.

Effects of the leading constituent on the composition of the rare earths are conspicuously manifest also in the isostructural minerals of the zircon group (zircon, xenotime, thorite) where the coordination number of zirconium and of its element-analogues (Sc, Y, U, Th) equals 8. Characteristically, in zircon, ZrSiO_4 , the rare earths are chiefly of the cerium type and are enriched in the lanthanides (Yb, Er, Dy) whose ionic radii are close to that of Zr. Zircon is often enriched also in thorium which resembles the lanthanides.

Thus the leading constituent of xenotime, $(\text{Y}, \text{Dy}, \text{Yb})\text{PO}_4$. The rare earth peaks in this mineral are at Dy and Yb—the elements whose ionic radii are similar to the ionic radius of Y.

Similarly, thorite, ThSiO_4 , is often enriched with the cerium rare earths whose ionic sizes are not greatly different from that of Th ion. This shows that, in rare-earth bearing minerals of the same structural type, the rare-earth composition is dependent significantly on the ionic size of the leading constituent whose coordination number is the same as of the rare earths.

Characteristicly, the rare earths have a cerium composition in monazite, ThO_2 , here investigated, whereas in uraninite, UO_2 , isomorphous and isomorphous with thorianite, their composition is altogether different and has its maximum at Gd and Dy, the lanthanides resembling uranium in their ion size. At the same time the possibility of substitution of any lanthanide by ThO_2 or by UO_2 has been proved experimentally.

Thus we have an outline of a picture of an isomorphous "co-optimal" admixture (apparently also of a still greater endocryptic one) of the leading constituent, on the principle of similarities of ionic radii.

The incommensurability of the molecular quantities, let us say, UO_2 and RE_2O_3 , probably is also expressed, in this connection, as the "assimilation of the minority by the majority."

The associations of isomorphous constituents wherein the lanthanides are included are characteristic. We had already spoken of the selective cerium rare earths associated with Sr, Ba, Na in minerals (nordite, loparite, etc.). The association with U is characteristic for Gd-samaraskite, obruchevite (yttrian pyrochlore), uraninite. Minerals that are high in Nd are the richest in thorium. Such are the Nd-aeschynite and the poorly selective cerium compositions of monazite. Conversely, thorium minerals (thorite, thorianite) are rich in neodymium. Britholite, a cerium mineral, is enriched in thorium. At the same time, its yttrium analogue, abukumalite, is enriched in iron and manganese.

Iron is replaced by the yttrium earths in siderite, FeCO_3 . Thus Sr, Ba, K, Na minerals are generally selective for the cerium earths and Zr, Sc, Fe, Mn minerals are generally selective for the yttrium earths. Calcium minerals are of the complex type in respect to the rare earths.

In regards to the "co-optation" of the rare-earth admixtures, calcium is selective to a much lesser degree than, let us say, Zr, Sc, and Fe whose ionic size resembles only the restricted group of the smallest ions of the yttrium earths. Although the yttrium composition of the rare earths is more characteristic for zircon, there are also zircons with cerium or with neodymium maxima (No. 76). Such "complexity" of zircon, with respect to rare earths, is related to the intermediate magnitude of the coordination number, 8, which is more specific for the complex than for the selective mineral types. Some specific features of the composition of zircon—subject to variations within a wide range (enrichment with Fe, Th, U, Hf, Sc)—may play a part in determining composition of the rare earths in this mineral. Thus an ytterbium maximum of the lanthanides may be a characteristic only of cyrtolites and not of any zircon. We must also take into account the possible expressions of some endocryptic phenomena (for example, the formation of the tetragonal variety of CePO_4 which is not found in ordinary environments) or the possibility of an uncommon assortment of anions (for example, the formation of CeNbO_4).

Classification of the rare-earth minerals merely as "selective" or as "complex" appears to be still too crude. Minerals within either of these categories still differ substantially from each other in regard to their capacities for isomorphism. Thus, although in selective yttrium minerals the rare-earths maximum falls invariably on Y, the lanthanide curve maximum is subject to a considerable change. Both Yb and Dy maxima are known in xenotime. Yb maximum is more characteristic for fergusonite, on the other hand.

It is evident that the selectivity of fergusonite is greater than of xenotime. A. I. Komkov [4] had shown recently that as a rule, rare earths have six-fold coordination in fergusonite. Their coordination

is 8 in xenotime, however. This may have a bearing on the fact that the rare-earths maximum in fergusonite falls generally on Yb, the smallest ion among the lanthanides, whereas the rare-earths maximum in xenotime falls both on Yb and Dy. The lanthanide maximum in teitite is invariably on Yb. It appears that minerals of such type may be classed together into a special subgroup of the selective yttrium-ytterbium type.

These selective cerium minerals also differ among themselves in the degree of their selectivity. Thus the Ce maximum in bastnaesite, one of the most definitely selective minerals, is never below 45, whereas the lower limit of cerium content of monazite may be as high as 41.5. The difference between bastnaesite and monazite is made especially apparent if we compare the range of variations not of their Ce maxima but of their La maxima (as lanthanum is the odd element related to cerium). This La range is 42.9 to 25 for bastnaesite but is appreciably lower for monazite: 37.7 to 13.1. The lower limit of this range is characteristic for the given mineral.

These selective minerals may be characterized also by the average compositions of their rare earths. For example, the bastnaesite average based on 10 analyses is: $\text{La}_{32.9} \text{Ce}_{50} \text{Pr}_{4.2} \text{Nd}_{11.8} \text{Sm}_{0.9} \text{Gd}_{0.2}$, while the monazite average based on 70 analyses is: $\text{La}_{24.5} \text{Ce}_{45.2} \text{Pr}_{5.2} \text{Nd}_{19.0} \text{Gd}_{2.2}$. It is evident that bastnaesite is more selective than monazite, by comparison of these averages.

Bastnaesite, nordite, fluocerite, and analogous minerals may be grouped together as an independent subgroup of the markedly selective minerals. The dividing line between the markedly selective and the selective minerals is defined by the lower limit of variation of the rare-earths maximum. This lower limit is taken conventionally at 45, so, minerals whose rare-earths maximum never falls below 45 (with the odd elements maximum—lanthanum—not lower than 25) may be classified with the markedly selective ones.

The selective yttrium-ytterbium minerals form a specific markedly selective yttrium group. We know of no other markedly selective minerals besides the cerium and the yttrium subgroups. Characteristically Yb and Yb occupy the extreme positions in the even lanthanide series. Both of these elements have only one competing neighbor, cerium, and not two like the rest of the lanthanides.

According to the classification, bastnaesite may be defined as a markedly selective cerium mineral, with the lower limit at $\text{Ce}_{45} (\text{La}_{25})$, and monazite, as a selective mineral with the lower limit at $\text{Ce}_{41} (\text{La}_{13})$. These minerals may be characterized also by their rare-earths compositions.

Complex minerals also differ among themselves in their capacity for selectivity, with the understanding that such minerals, by definition, are those in which the rare-earth composition maxima are subject to variation. For example, there are known gadolinite specimens in which the maximum falls, by turn, on practically every one of the even elements: Nd, Gd, Dy, Yb, while allanite contains the cerium rare

earths, in the vast majority of the cases. Only in one proved instance (yttrialite) did this mineral have its rare-earths maximum fall on Y (and Dy). Only Ce and Nd maxima are known for aeschynite (and probably also for thorianite). The extent of selectivity of gadolinite appears to be significantly smaller than that of aeschynite and allanite.

Some interesting results were obtained on a calculation of the mean effective radius of the rare earths in gadolinite. It developed that, despite an appreciable change in the position of the maximum, the mean radius was about the same for all of the compositions. The range of variation of the mean radius is narrow, even for gadolinite: 0.92 to 0.93 Å, that is, from Gd to Dy.

The point is that the high complexity of gadolinite, even with the maximum at ytterbium, results in a significant averaging-out both of the composition and of the mean radius of the rare earths. The mean radius is subject even to a smaller variation, in the case of the selective minerals. For example, this radius is about the same as the radius of Er in xenotime, for all compositions whose maxima are at Dy and at Yb. Such a narrow range of fluctuations of the mean radius, accompanied by a much wider range of variations in the positions of the maxima, may be explained by the commonly limited and narrow range of variation in the volume of the unit-cell. The composition of the rare earths "adapts itself" to this latter range, so as not to transgress the permissible boundaries, with the resulting minor changes in the mean radius of the group. Both the range of variation in the mean effective radius of the rare earths and variations in the positions of the maxima may serve to characterize the complex minerals. Thus gadolinite may be defined as a complex mineral, with the maxima at Y(Dy, Yb), Gd, Nd, and the mean radius between Gd and Dy. Inasmuch as the yttrium compositions are markedly preponderant in gadolinite, this mineral may be called a complex mineral with an yttrium tendency. Allanite may be called a complex mineral with a cerium tendency, because of its cerium composition, in the vast majority of cases.

The relationships governing variations in the composition of the rare earths in minerals, as clarified in the foregoing discussion, compel us to reexamine the system of chemical symbols employed in the mineral formulas. There is a great deal of obscurity, in this connection, in modern manuals and textbooks of mineralogy. For example, the formula of bastnaesite is given as (Ce, La, Pr) CO_3F . And yet, as a rule, there is more Nd than Pr in bastnaesite. The formula of fergusonite is given as (Y, Er, Ce) NbO_4 . The Er symbol is introduced into the formulas of many other yttrium minerals (churchite, hellandite, samarskite, euxenite) although all of them show Er minima, and not maxima on their composition curves for the lanthanides. By indicating Ce, alongside yttrium, in the formulas for fergusonite, euxenite, etc., we give the impression that these minerals belong to the complex type, whereas, in reality, they belong to the selective yttrium type.

In our view, it should be enough to give the symbol of only one of the elements—whose content is at the maximum—in formulas of the

ve minerals. Thus samarskite, churchite, bastnaesite should be respectively as $(\text{Gd}, \text{U}, \text{Fe}^{2+}) \text{Nb}_2\text{O}_6$, $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$, CeFCO_3 . The symbol, TR ("terrae rarae," the rare earths), in the sense of atoms and not of their oxides, should be employed advantageously in cases of the complex minerals. Thus the formula of gadolinite may be $\text{TR}_2\text{FeBe}_2\text{Si}_2\text{O}_{10}$. In case some individual element is preponderant it ought to be rational to indicate this by its symbol. Thus allanite may be written as $(\text{TR}, \text{Ce})\text{CaFeAl}_2(\text{Si}_3\text{O}_{12})(\text{OH})$ and the special case of the enrichment of gadolinite with yttrium may be represented as $(\text{Y})_2\text{FeBe}_2\text{Si}_2\text{O}_{10}$.

Studies of relationships governing the distribution of rare earths in minerals enable us also to approach the problem of systematics of the rare-earth minerals—a field wherein confusion still reigns. A separate designation has been proposed for abukumalite, $\text{Ce}_6\text{O}_{24}(\text{OH})_2$, which is the yttrium analogue of britholite, $\text{Ca}_4\text{Ce}_6(\text{OH})_2$, relegating abukumalite to the status of an independent mineral. The same applies to yttrocerite, $(\text{Ca}, \text{Ce}) \text{F}_{2-3}$ and yttrofluorite, $(\text{Ca}, \text{Y})\text{F}_{2-3}$. In other instances, however, structural analogues existing only in their rare earth compositions were regarded as mere varieties (cergadolinite, yttro-orthite).

The foregoing data on the rare earth compositions of gadolinite show that in addition to the ordinary yttrium gadolinite, it is possible also to recognize neodymium and gadolinium gadolinites, depending on the position of the maxima. Neodymium aeschynites may be similarly distinguished among the commonly cerium aeschynites. It is possible that these minerals (Nd and Gd gadolinites; Y allanite; Nd aeschynite) deserve recognition as independent minerals as well as designation of independent names, very much like the niobium and the tantalum analogues columbite and tantalite, etc., had acquired their separate recognition. Indeed, the Nd aeschynite is an end-member of the possible isomorphous series: Ce aeschynite (CeNbTiO_6)—Nd aeschynite (NdNbTiO_6), and Nd are entirely independent elements, notwithstanding their resemblance, like Nb and Ta. Moreover, in addition to the full isomorphism involving members with different positions of rare-earths maxima, there may be also an incomplete and partial isomorphism entailing a more or less extensive field of immiscibility. Therefore, it appears hardly feasible to differentiate such a large number of independent rare-earth minerals. This would serve merely to complicate the mineralogic nomenclature. The minerals in question are studied very poorly. Also, there are only minor differences between the properties of Nd and Gd gadolinites, for example, and the properties of ordinary yttrium gadolinite, inasmuch as all of the rare earths resemble one another very much in their properties. Consequently, minerals whose structures are the same as the structures of the prototype but whose rare-earths maxima differ from their prototypes are here suggested for the consideration as varieties. Nd and Gd gadolinites belong to this category (as varieties of gadolinite), as well as Nd aeschynite and the Y allanite. Even under such conditions,

abukumalite must be regarded as an yttrium variety of britholite (as Y britholite), and ytthrofluorite as an yttrium variety of ytthrocerite (Y ytthrocerite). The latter designation is awkward and it should be reasonable to find another name for ytthrocerite. Then ytthrofluorite and ytthrocerite could be regarded as yttrium and cerium varieties of this newly named mineral.

Inasmuch as the rare earth composition constitutes a definite characteristic of minerals, especially of the selective ones, it is suited for the diagnosis and identification of minerals.

In such manner, G. P. Barsanov [5] suggested that khlopinite is an analogue of samarskite, on the basis of his x-ray analysis of its structure. The fact that both of these minerals have the same gadolinium maximum, among their lanthanides, is clear evidence supporting his suggestion. The "ampangabeite" from the pegmatites of Madagascar is also a samarskite. This is indicated by the resemblance between the diffraction patterns of these two minerals and by resemblance between the gadolinium maxima of their rare-earth compositions (No. 44). However, the "ampangabeite" from the Ukrainian pegmatites (No. 48) is a euxenite, judging by its diffraction patterns and by the yttrium-ytterbium character of its TR.

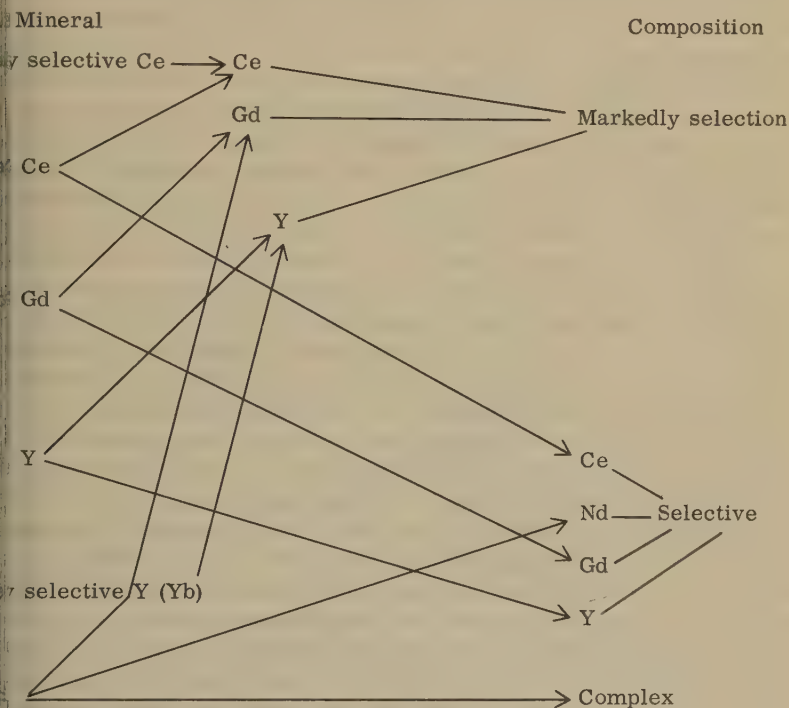
We know of the opinion, based on x-ray analyses, to the effect that "yttrotantalite" is an analogue of fergusonite. The fact that the lanthanides of "yttrotantalite" and of fergusonite have the same ytterbium maximum supports the validity of this opinion. The neodymium maximum of the lanthanides in lyndochite, established by Butler [6], is an indication that lyndochite is closer to aeschynite than to euxenite. The resemblance between the rare earths of toernebohmite and cerite, of blomstrandine and euxenite, is an important argument in favor of identity of these minerals. If the number of minerals belonging to the same type is not too great, it is possible to determine the character of the given mineral by the composition of its rare earths. Thus, a marked gadolinium maximum among the rare earths of the mineral in question justifies a supposition that this mineral may be a samarskite; if the rare earth composition is of the complex cerium-neodymium type, the mineral may be an apatite-phosphorite.

In order to characterize a definite specimen of a rare earth mineral, we must know its actual composition, in addition to its isomorphic capacity and the possible range of variation of its rare-earth content. Indeed, the crystallochemical structure of the mineral predetermines its possibility of having this or that type of the rare-earth composition, whereas its actual composition, within the possible limits is determined by the proportions of the rare earths in the original solution or the original melt.

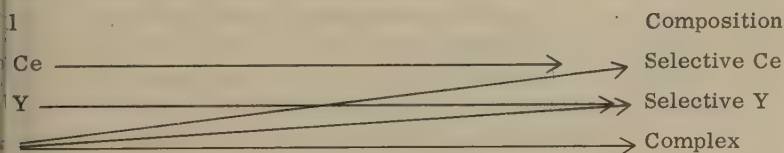
A markedly selective mineral may have only a markedly selective composition. A selective mineral may have either a selective or a markedly selective composition. Finally, a complex mineral may have any type of the composition: complex, selective, or markedly selective.

Classification of the rare-earth minerals must take into account the composition of the rare-earth compositions.

For the markedly selective and the selective minerals and compositions are by no means known, at present, for all of the even lanthanides, the relationship in question may be represented as follows:



According to analytical Table [1], the minerals are grouped in accordance with this particular classification (the rare-earth minerals-proper are ahead of the "titular" rare-earth minerals). By omitting from consideration the unique gadolinium and neodymium selective mineral compositions, the following very simple schematic arrangement may be offered:



According to this classification, the monazite specimen (No. 29), containing 38% La_2O_3 and 49% CeO_2 , as of its total rare earths, may be classified as a selective cerium mineral of a markedly selective

character. The specimen of Y-allanite (No. 91) may be identified as a complex mineral of a selective yttrium composition.

The fact that the characteristics of the minerals themselves, their isomorphous capacity, and the specific features of their rare-earth composition are described by the same terms, "selective" and "complex," in the classification here discussed, is embarrassing. It should be possible to choose some independent terms out of these two categories of concepts.

V. M. Goldschmidt [7] had given the classification of rare earths. He did not consider, however, the classification of rare-earth minerals. Types of rare-earth compositions were distinguished by Goldschmidt by their minerals (monazite, allanite, yttrio-fluorite, xenotime, thortveitite). K. Rankama and T. Sahama [8] suggested still another type of the rare earths: wiikite.

Were we to follow this line of development, we should be led to recognize a whole series of additional types: aeschynite (with a conspicuous Ce maximum), phosphorite (with practically equal Nd and Ce maxima), etc. Such paths appear to us to be incorrect, however. Indeed, the rare-earth compositions of many mineral specimens display certain characteristic features that could be used as reasons for creation of more and more composition types with independent designations. However, the type designations would be assigned on the basis of the minerals, whereas the minerals themselves would remain by no means constant in their rare-earth compositions. We would find ourselves therefore referring to an allanite of the yttrium composition as a mineral of the xenotime type, and to an allanite of the selectively cerium composition as a mineral of the bastnaesite type, etc., and calling some other minerals (cerite, rinkolite) varieties of allanite. Such practices would lead only to confusion. The previously suggested classification of the rare-earth minerals and compositions, based on positions and magnitudes of the maxima of individual lanthanides, within their limits of variation, is definitely more feasible.

Although complex minerals may have any type of the rare-earth composition in theory, their actual rare-earth composition is of the complex type, in the majority of the cases. In a similar way, they have generally a selective but not the markedly selective composition. The complex composition here means that all of the lanthanides are more or less equally well suited for the structures of the given mineral wherein their proportions depend on their clark ratios in the given solution or in the given melt. It is in this very relationship that the deficiencies of Sm, Eu, Er, Tm and the preponderances of Ce, Dy, etc., become manifest. The rare-earth compositions of complex minerals reflect the proportions of the lanthanides in the original solution to a far greater extent, it appears, than is indicated by the compositions of selective minerals. Consequently, in our studies of such proportions in rocks, we must be guided especially by the rare-earth compositions of complex minerals which are, in a way, indicators of environments.

plies evidently not only to the rare earths but also to other isomorphous elements: Ca - Sr, Ti - Nb, and others.

Structures of the markedly selective minerals permit the entry only of a narrowly defined group of the rare earths whose properties are similar. The other lanthanides are "dragged" into the mineral structures, endocryptically and in small quantities, by the leading elements entirely because their properties are similar to the properties of the leading elements. The Clarke proportions of the lanthanides in rocks become unimportant, in such environments, and they function only as corollaries. Consequently, there are no supplementary elements, in the instance of the deficient Tm, Sm, Eu, etc., and the characteristic lanthanide proportions are disturbed accordingly.

In such manner, composition of the rare earths in complex minerals is determined essentially by their composition in the original solution, or melt; in the case of selective minerals, however, it is determined by their limited capacity for the isomorphism, once the selective minerals had made their appearance. However, crystallization of complex and selective minerals of different kinds is determined by environments of their origins.

The initial rare-earth composition, in the melt-solution, remaining in solution after the saturation of the isomorphic and the endocryptic capacities of the Ca, Th, Zr, Fe, etc., rock-forming minerals, with respect to the rare earths, has an important effect on the associations of rare-earth minerals. For example, in deposits related to alkali feldspars, ijolites, nepheline and alkali syenites, the initial solutions are markedly enriched in the selective cerium minerals (loparite, norcyclyte, steenstrupine, etc.). Complex rare-earth minerals and rock-forming minerals show also the cerium composition of the rare earths. So far, not a single yttrium mineral could be found in such environments, although the yttrium-type composition of the monazite has been reported—only in zircons—on account of the resemblances between Y and Zr. Small amounts of the yttrium earths, present in the original solutions, had entered the cerium minerals endocryptically and they had entered also the complex and the calcium minerals. This may be explainable by the phase rule, by the tendency toward the least possible number of the minerals in the system.

In the case of granite pegmatites in which a drastic enrichment with rare earths had resulted in the formation of an association of selective cerium minerals (fergusonite, yttrialite) and of complex minerals of yttrium composition (gadolinite). However, the more common granite pegmatites and hydrothermal deposits contain associated selective cerium minerals (monazite), selective yttrium minerals (xenotime, etc.), and complex minerals (gadolinite, allanite). In such instances, the complex material of a complex-intermediate composition may in places replace both a selective cerium and a selective yttrium mineral in the rare-earth series, and to inhibit their formation. We must consider, however the role of anions, in this connection, which must be necessarily present in their "required assortment."

Clearly, the presence of large amounts of Ca, Th, Zr, Fe minerals and their well defined capacity for isomorphism, with respect to rare earths, is conducive to their dispersion as it prevents formation of independent rare-earth minerals.

In the case of an enrichment of the rocks with respect to zircon, which often absorbs the yttrium rare earths selectively, the other minerals of the rocks may become enriched in the cerium rare earths.

A definite relationship may become established in some instances between rare earths in different minerals crystallizing from one and the same solution. Thus from the published [9] rare earth composition in xenotime and allanite from one and the same pegmatitic vein, it is evident that, if the allanite has an emphatically selective composition of the cerium type, the rare earths of the xenotime show a dysprosium maximum (Tedino, Karelia). If, on the other hand, the allanite has but a weakly selective composition, of the cerium type, and is enriched instead with neodymium and the heavy lanthanides, the rare earths of the xenotime acquire an ytterbium maximum (Ytterby, Sweden), inasmuch as the intermediate lanthanides had already entered the allanite. There develops a synchronous shift accordingly, in the rare earths both of the cerium and of the yttrium mineral (to the right and to the left of the rare-earth series in the periodic table), when several rare-earth minerals are being formed simultaneously. There develops also a certain tendency toward a dependence of the composition of the rare-earth minerals on their genetic environment. Thus, in the supergene minerals (rhabdophanite, halloysite, phosphates) a europium "high" has been observed in many cases (Sm/Eu about 5, instead of the common 20 to 30), as well as a lanthanum "high" (to the point of $\text{La} > \text{Ce}$).

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SHIFTS OF ISOTOPIC RATIOS IN
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Abstract

Modification of the method for the determination of UI and UII has been carried out and a shift of the isotopic uranium composition in laboratory conditions has been obtained.

As much as the migration of radioactive elements in natural environments depends on a number of variables, it is reasonable to reduce the number of such variables, in our studies of the migration, in order to ascertain their individual roles with greater clarity. In studies of this type, inquiries into mobility of individual isotopes of one and the same element are especially worthwhile because they serve to equalize chemical and the crystallochemical distinctions while making distinctions due to their radioactive properties conspicuously manifest. Investigations along these lines were begun by I. E. Starik and co-workers [1, 2, 3, 4, 5, 6, 7] in 1930 and are still in progress. V. V. Cherdyntsev [8, 9] has suggested the methods in the course of this research and has determined the UII and UI isotope ratios in certain natural materials. A substantial enrichment with UII was discovered in several instances, particularly in a specimen of schroekingite. By agreement with V. V. Cherdyntsev we carried out the more exact determinations of the isotopic ratios of uranium in certain minerals and in solutions by which these minerals are being leached. According to V. V. Cherdyntsev's procedure, the UII and UI ratio is determined by measurements of the α and of the β -activity of radiochemically purified uranium. The β -activity, which depends on the activity of UXII or, more exactly, of UXII in equilibrium with UXI, is the criterion of UI. The α -activity is the criterion of the sum of UII and UI. The defect of this procedure is the low accuracy of the determination due to inexact measurements of the weak β -activity. We modified this procedure. Inasmuch as the half-life of UII is appreciably shorter than the half-life of UI, the weight-proportion of UII compared to total uranium is insignificantly small, and the weight of uranium is a direct measure of UI. The α -activity is still the criterion of the sum of UI and UII. As much as quantitative determinations of uranium (gravimetric or spectrographic) are considerably more accurate than the β -activity

measurements, the amounts of uranium being the same, the method here proposed is more exact.

The procedure for determining the proportions of UII and UI consists therefore of a careful radiochemical purification of uranium, its quantitative estimation, and the measurement of its α -activity. In the radiochemical purification, the isotopes of thorium were removed by coprecipitation with cerium fluoride and the isotopes of radium by coprecipitation with BaSO_4 ; Po was removed electrolytically. In several cases this purification was replaced by the extraction of uranium from the test solutions with ether.

Table 1

Material	Age	Amount of uranium in target, mg	α -activity, impulses per minute	UII/UI
Uranium nitrate	---	1	730 ± 8	1
Uraninite	Archean	1	730 ± 8	1
Pitchblende	Caledonian	1	710 ± 8	1
Pitchblende ore	Harz	1	720 ± 8	1
Schroekingerite	Quaternary	1	1490 ± 15	3.1(3.7)*

*According to V. V. Cherdyntsev

Table 2

Mineral	Leaching solution	Time of leaching	Quantity of uranium in target, mg	Impulse activity minutes/mg	UII/UI
Pitchblende	0.0001 N HNO_3	13 months	1.0	730	1.0
Pitchblende	0.1 N HNO_3	6 days	1.0	730	1.0
Pitchblende	0.01 N HNO_3	6 days	1.0	710	1.0
Pitchblende	0.1 N Na_2CO_3	6 days	1.0	730	1.0
Pitchblende	0.1 N Na_2CO_3	6 days	1.0	710	1.0
Uraninite from	0.0 N HNO_3	3 hours	0.77	717	1.0
Kamennaya Taibola }	0.1 N Na_2CO_3	3 hours	0.56	800	1.23
Uraninite from }	0.01 N HNO_3	3 hours	1.39	718	1.0
Chkalov Mine }	0.1 N Na_2CO_3	3 hours	0.287	762	1.13
Uraninite sublimated from pitchblende at 800°C .			0.12* ± 0.025	1471 ± 15	3.24*

*By the luminescence method.

Uranium is separated from iron and aluminum by means of ammonium carbonate. Uranium is determined quantitatively by a gravimetric method which may be replaced by a polarographic method if the amounts of uranium are small. The quantitative precipitation of uranium on the surface of stainless steel was carried out from 0.4 *M* ammonium oxalate solution in accordance with the procedure described by Hufford and [10]. The α -activity was measured in the DA type apparatus. The targets on which uranium was precipitated from uranyl nitrate solution were prepared in the same manner.

We examined some primary uranium minerals of different age as well as a secondary mineral, schroekengerite, placed at our disposal by V. V. Cherdyntsev, and we carried out some experiments with leaching of uranium by different solvents for different periods of time. The results are reported in Tables 1 and 2. As expected, the results in Table 1 show no shifts in the isotopic composition of uranium in primary minerals of an age sufficient for the attainment of the radioactive equilibrium. The shift in the isotopic composition of uranium in schroekengerite, noted by V. V. Cherdyntsev, was confirmed by us and the shift was measured with a greater exactitude.

The results in Table 2 indicate that the isotopic shift may be forced, even in a static leaching environment, only in a short-term experiment with a too active leaching solution. The shifts, however small, are detected only upon leaching of fairly well preserved minerals with 1 *N* Na_2CO_3 for 3 hours. This is due apparently to an active isotope exchange masking the original isotopic shift.

The last column in Table 2 shows the UI and UII proportions for uranium isolated from pitchblende by the sublimation procedure, as carried out in our laboratory for lead. Research has just begun on the problem of the isolation of uranium by this method and on the determination of its isotopic composition in the sublimation and it is not possible for that reason, to consider these magnitudes in greater detail in the present report. We may simply point out that the uranium here studied was isolated at 800°C and that uranium continues to be sublimed up to 1000°C but to a lesser degree than at 800°C. Above 800°C, however, uranium is subject to sublimation in appreciable amounts. There is a large error in the isotopic ratio, as here reported, because the determination of uranium was done by the luminescent method, the error of which is considered by us to be 20%. This method will be made more exact in the future.

Summarizing the foregoing findings, we may report that we developed an exact modified procedure for the determination of the UI and UII proportions and that we observed a shift in the isotopic composition of uranium under laboratory conditions in the leaching and in the sublimation methods.

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ISOTOPIC SHIFTS IN NATURAL
URANIUM COMPOUNDS

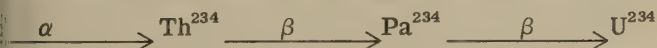
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Abstract

Isotopic shifts in natural uranium compounds have been studied according to the $^{238}\text{U}/^{235}\text{U}$ ratio in a leaching solution and residue for various fractions. The determination of the uranium isotopic composition has been carried out on a 50-channel apparatus for α -spectra measurements. The accuracy of the determination of the $^{234}\text{U}/^{238}\text{U}$ ratio is $\pm 1-2$ per cent. The preparation of uranium samples for α -spectrometric studies is described. It has been shown that uranium isotopic composition in natural materials can change as a result of secondary processes. By means of the described method for determining uranium isotopic composition the study of the uranium origin in various natural materials is possible.

It has been demonstrated recently, in several studies [1], that the isotopic equilibria of $^{234}\text{U}/^{238}\text{U}$ may be disturbed significantly in minerals and rocks. This phenomenon is due to the fact that the ^{234}U isotope is formed from ^{238}U , in consequence of a series of radioactive transformations, in harmony with the pattern of decay:



For that reason, ^{234}U may be less firmly fixed in the solid structures and may be more mobile accordingly. Such effects are entirely possible. However, since it was not possible for us to ascertain the reliability of the methods employed by the authors here cited [1], whose results were based on independent determinations of every one of the isotopes, it seemed desirable to undertake measurements of magnitudes of the isotopic shift in natural uranium by a direct method based on direct and simultaneous determinations of one of the uranium isotopes in a multi-channel apparatus. We examined chiefly secondary and redeposited minerals, where the isotopic differences could reasonably be expected, in our study of the isotopic shifts and of differences in mobility of the uranium isotopes. The specimens presently to be described were kindly placed at our disposal by members of the staff of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Academy of Sciences of the USSR: I. G. Chentsov, V. S. Serebrennikov, and G. A. Volkov.

I. URANIFEROUS SAMPLES

Samples 1 and 2: Pitchblende.

Sample 3: Water; high in uranium; same source as Sample 4.

Sample 4: Crusts and films of black substance on a quartz-sulfide vein. Sulfides are chiefly fine-grained pyrite and isolated inclusions of chalcopyrite; relics of pitchblende are visible in the black substance.

Sample 5: Films of black; soot-black and gray-black. Some quartz-sulfide vein as in Sample 4. Abundant limonite, forming fine films in the cracks; finest films of uranium sulfates are present, chiefly in association with the black substance. Relict pitchblende is not visible but may be present.

Samples 4 and 5 were taken from two different ore bodies, 220 m. apart, at one and the same deposit.

Sample 6: Films of black substance on fine grains of pyrite included in clayey matrix, in the sahlband part of the vein.

Samples 7, 8, 9: Ores of uraniferous bituminous limestones from Meso-Cenozoic beds. The ore minerals are "uranium black" and pitchblende. Uranium compounds, dispersed originally in sedimentary rocks, were redeposited and accumulated together with sulfides of heavy metals in places where accumulations of organic substance had previously occurred in the course of diagenesis and epigenesis. In Samples 7 and 8, a lesser part of uranium is associated with the carbonaceous organic substance of bituminous origin. In Sample 9, uranium is tied up with soft bitumens penetrating the rock through fissures. The bulk of uranium in Sample 9 was deposited epigenetically (sorption) by bitumens from underground (petroliferous) waters.

Samples 10, 11, 12, 13: Albitized limy tuffs enriched by phosphate (fluorapatite). The sedimentary uranium-phosphate ores, in all instances, were altered severely by a carbonate-alkali metamorphism. The phosphate substance of the ores has become segregated as crystals to a large extent, and it is pierced by microscopic veinlets of calcite, albite, and apatite. Locally, small amounts of zirconium silicate (malakon type) were added to the assemblage of these minerals. No independent uranium minerals could be found in the ores; 80 to 95% of their total uranium is accumulated in the apatite concentrate and about 10% (in the clay mineral fractions) in hydromicas, with a small amount of uranium in the zirconium minerals. As a rule there are several times as much uranium in the apatite of the veinlets as in their phosphate-bearing host rock. Samples 10 and 11 are noticeably different from Samples 12 and 13. The former are more altered by the carbonate-alkali epigenesis. An appreciable proportion of uranium in Samples 10 and 11 was deposited after the formation of the uraniferous primary phosphates, i.e. were supplementary accessions from solutions that had penetrated the phosphate rock (possibly hydrothermal solutions).

II. TREATMENT OF URANIFEROUS SAMPLES

ick samples used in the determination of the isotopic composition nium were fragmented to about 2 to 3 mm maximum particle size re separated into mechanical fractions by screening. The sam- o prepared were treated by solutions consisting of dilute hydro- acid (1:16) and 0.3% hydrogen peroxide (for silicates) or 0.002 *M* n citrate and 0.6% hydrogen peroxide (for carbonates). The ents were in static environments. Duration of the treatments o to 27 days. After the end of the treatment, the solution was oted from the residue and the residue was treated with concen- hydrochloric acid with 1.5% hydrogen peroxide, followed by heat- h aqua regia, for the isolation of uranium.

m the solutions so obtained [2], uranium was isolated as follows: lution was evaporated to dryness. The residue was taken up with nitric acid and magnesium nitrate to make their concentrations nd 2.5 *M* respectively. Uranium was extracted from the result- lution by two equal volumes of ether (in succession). The ether as separated and was washed with a saturated solution of mag- nitrate. The washed ether was evaporated to dryness in the ce of hydrochloric acid. The residue was taken up in 8 *N* hydro- acid and the traces of iron were extracted with an equal vol- amyl acetate. The hydrochloric acid solution was passed n a chromatographic column filled with anionite of the Daeuks-1 The anionite was washed with 8 *N* hydrochloric acid and uranium eached out with 0.5 *N* hydrochloric acid. The leachate was evap- to dryness and the procedure was repeated. The resulting solu- as evaporated to dryness with nitric acid and the dry residue was ed in 4.5 mls of 1 *M* solution of ammonium acetate. 10 mls of as was added for the electrolytic precipitation of uranium [3].

electrolytic precipitation was done at 60°C, and 2 to 3 m.a./cm² t density. The anode was a spiral of platinum wire; the cathode- of stainless steel 40 mm in diameter. Duration of the electro- depended on concentration of uranium in the solution and was 0 minutes per 0.5 mg uranium.

samples prepared in such manner proved to be entirely suited alpha-spectrometric determinations of the isotopic composition nium.

III. ALPHA SPECTRA MEASUREMENT TECHNIQUES

ased the 50-channel apparatus for measurements of α -spectra studies of the isotopic composition of uranium. A general view apparatus is shown in Figure 1 and its block-diagram in Figure 2. apparatus consists of an ionization chamber, with a pre-ampli- linear amplifier with a discriminator; and amplitude analyzer of

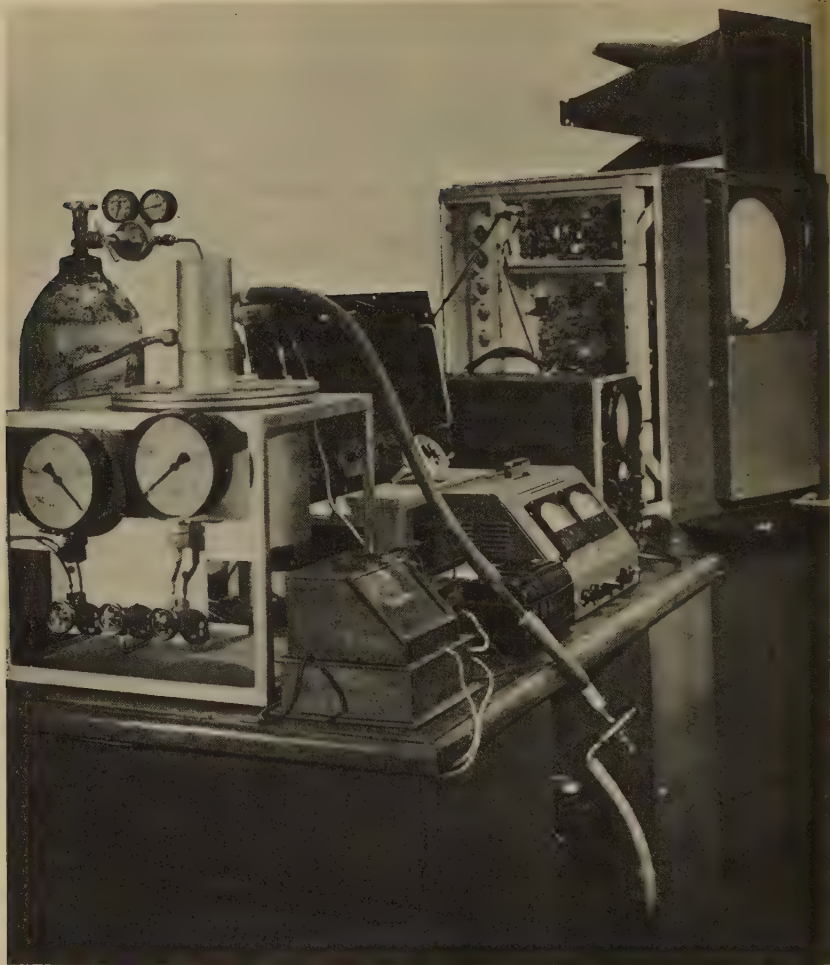


Fig. 1. General view of installation for measurements of α - spectra.

the impulses; a source of high tension current; sources of feed for all of the blocks; a gas-filling set-up for the chamber.

The ionization chamber is operated on ionic impulses. The collector-electrode is a ball 8 mm in diameter placed inside a latun* cylinder ($d = 150$ mm; $h = 160$ mm.) The chamber is evacuated to about 0.1 mm Hg pressure by the means of a fore-vacuum pump and is filled by argon to the atmospheric pressure. The test samples are placed in a special holder at the floor of the chamber. Mechanical collimators are used in order to improve the resolving capacity of the chamber.

*Cu-Zu alloy? VPS

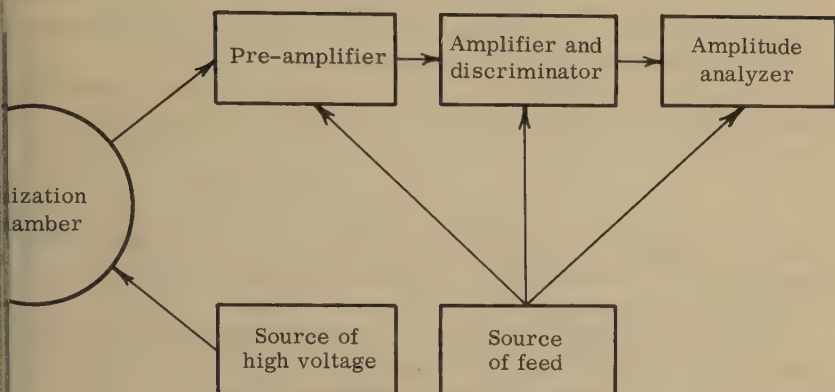


Fig. 2. Block diagram of installation for measurements of α -spectra.

ension is fed to the high-voltage electrode from batteries and is to about 2500 volts in the case of the chamber here used at the ted pressure. Not more than 10 minutes is required in order to the chamber ready for the measurements.

e set-up was operated on ordinary principles. Impulses from the tor electrode in the chamber are fed to the pre-amplifier placed ly on the chamber. The gain of the pre-amplifier is about 50. mplified impulses are fed to the main linear amplifier which has le gain (10^3 to 10^5). The impulses, at the amplitude of about 100 are fed from the outlet of the linear amplifier to the 50-channel se amplitude analyzer whose basic construction was described in lier publication [4]. The filaments of the pre-amplifier are heated he rectifiers and the voltage is controlled within ± 0.05 volts; the ents of the linear amplifier are also fed by direct current from the ally designed 6 volt rectifiers. The rest of the blocks have ordi- systems of filament and anode supply.

e measured α -spectrum is recorded by the impulse-amplitude er in an ordinary oscillographic tube. The spectra are either ed visually or are recorded on a film for their subsequent treat-

ure 3 shows the spectra of uranium samples, as determined in apparatus, for the enriched (Fig. 3a), the equilibrium (3b), and the erished (3c) content of U^{234} . The basic principle of recording spectra of α -particles is indicated in Figure 3d.

IV. TREATMENT OF DATA

more than 150 α -spectra were recorded and analyzed in our studies isotopic composition of uranium. Every one of the U^{234}/U^{238} ra- reported in the Table is based on 3 to 5 replicate analyses either

of aliquots of one and the same sample or of identically processed replicate samples. The probable errors of the measurements were calculated as follows (see, for example, [5, 6]):

The standard deviation of the N_2/N_1 quotient is determined from the statistical errors in the measured number of the impulses in every peak:

$$\sigma_X = (N_2/N_1) \sqrt{\sigma_1/N_1)^2 + (\sigma_2/N_2)^2} \quad (I)$$

where N_1 and N_2 are the numbers of particles of U^{238} and U^{234} respectively, and σ_1 and σ_2 the corresponding statistical errors in the N_1 and the N_2 magnitudes.

Having determined the statistical weighed means for several measurements in one and the same sample, by the equation:

$$\omega_1/\omega_2 = \sigma_{X_2}^2/\sigma_{X_1}^2 \quad (II)$$

where ω is the statistical weighed mean value of the σ_X , we find the arithmetical mean for the sum total of the measurements:

$$\bar{X} = \frac{\sum \omega(N_2/N_1)}{\sum \omega} \quad (III)$$

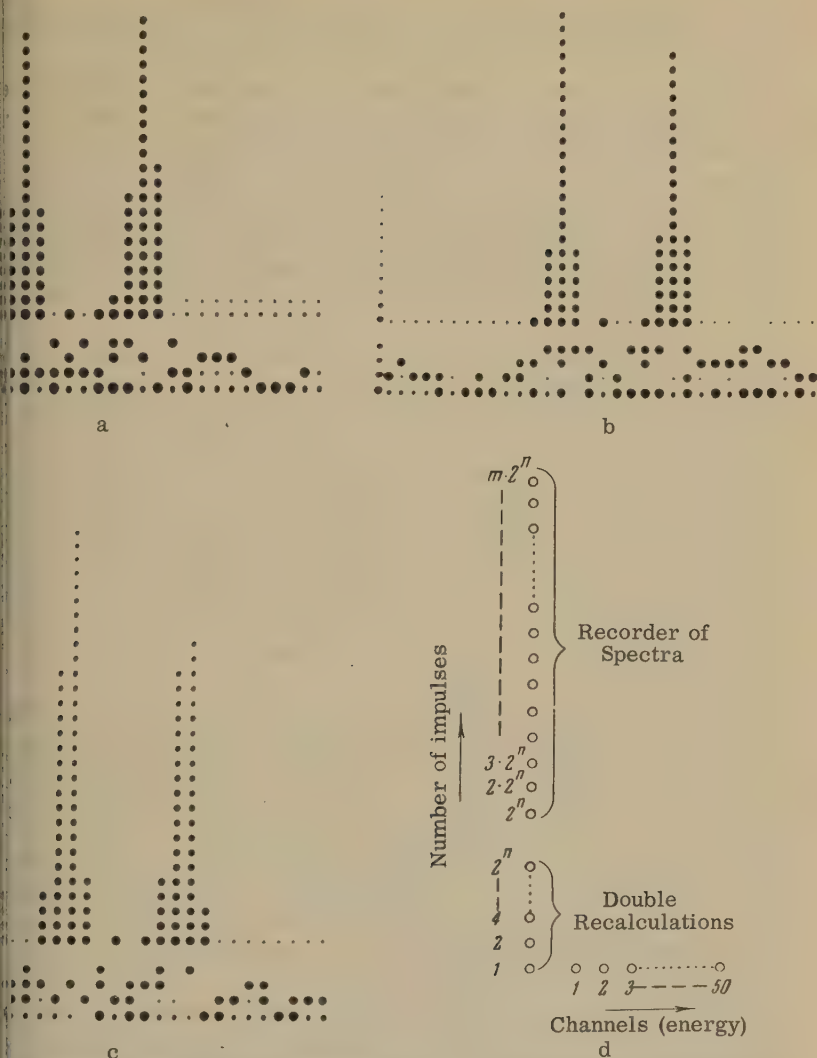
Finally, we find the probable error of \bar{X} , by the equation:

$$P_{\bar{X}} = 0.67\sigma_X = 0.67 \frac{\sigma_X}{\sqrt{\sum \omega}} \quad (IV)$$

The probable errors in the U^{234}/U^{238} ratio, as calculated, are reported in the Table. There may be also errors in the absolute magnitudes of the U^{234}/U^{238} ratio (in addition to the errors shown in the Table) in the vicinity of 1 to 2% originating in the processing of the determined α -spectra.

Sample No.	Material	Medium	U^{234}/U^{238} ratio					
			Particles < 1 mm		Average sample		Particles < 0.15 mm	
			Leachate	Residue	Leachate	Residue	Leachate	Residue
1	Pitchblende	-	-	-	0.98±0.02	-	-	-
2		-	-	-	1.03±0.01	-	-	-
3	Water	-	-	-	1.11±0.02	-	-	-
4	"Uranium Black"	HCl + H ₂ O ₂	-	0.97±0.02	0.98±0.02	0.97±0.02	1.06±0.03	0.96±0.02
5			0.97±0.02	0.89±0.01	0.97±0.02	0.96±0.02	0.95±0.02	1.13±0.01
6		Ca citrate + H ₂ O ₂	1.08±0.05	0.92±0.02	-	0.99±0.02	-	-
7	Uraniferous bituminous limestone	Ca citrate + H ₂ O ₂	0.91±0.01	0.91±0.02	0.94±0.02*	1.00±0.02*	-	-
8			0.89±0.02	1.03±0.02	0.88±0.02	1.00±0.02	-	-
9			0.98±0.03	1.05±0.02	1.04±0.04*	1.10±0.02*	-	-
10	Phosphate-rich albitized limestone tuff	Ca citrate + H ₂ O ₂	-	-	1.34±0.03	0.94±0.04	-	-
11			-	-	1.27±0.03	0.99±0.04	-	-
12			-	-	1.07±0.04	0.91±0.03	-	-
13			-	-	-	1.03±0.03	*	-

*The average sample does not include particles smaller than 1 mm.



Alpha spectra of uranium samples (a, b, c) and system of recording of (d).

V. DISCUSSION

ts on the U^{234}/U^{238} ratio are reported in the Table. It follows findings that the isotopic composition of uranium in natural is indeed subject to change. There is isotopic equilibrium U^{234} and U^{238} (Samples 1 and 2) in the pitchblende. In the case "black," there are possibilities for an equilibrium ratio of isotopes, as well as possibilities for a relative enrichment

or impoverishment of the U^{234} isotopes (Samples 4, 5, 6), in a possible relation to the origin of the "uranium black." The uranium-high water (Sample 3) is enriched with respect to the U^{234} .

In some instances isotopic changes in the composition of uranium are related probably to the effects of petroliferous waters which is expressed in the relative increase of the U^{234} content, parallel with the increase of the uranium fraction fixed in the organic substance (bitumens), as well as in the relative decrease in the U^{234} , parallel with the increase in the uranium content of the pitchblende and of the "uranium black" (Samples 7, 8, 9). It should be pointed out that the average isotopic composition of uranium in our samples is either close to equilibrium or at equilibrium.

As to the isotopic composition of uranium in the leachates, it should be noted that it corresponds inevitably to the isotopic composition of uranium in the samples. It is possible that the leachate carries not only the uranium derived from decomposition of the minerals or from radioactive processes but also uranium that was captured by rocks from the waters, in one way or another. Thus, for example, the uraniferous phosphates affected by the hydrothermal solutions (Samples 10, 11) show a higher U^{234}/U^{238} ratio, both at equilibrium and at the somewhat isotopically impoverished composition of the residue, whereas the isotopic composition of uranium in the leachates of the phosphate rocks which were not affected by hydrothermal solutions is very close to isotopic equilibrium (Sample 13).

Even if the average isotopic composition of uranium in natural materials corresponds to isotopic equilibrium, the isotopic composition of uranium in different fractions of one and the same sample (Sample 5) may not be the same, as shown by results on the isotopic composition of uranium in different mechanical fractions of the sample. This difference may be related possibly to a redistribution of uranium in secondary processes. Thus it is evident that, in the case of samples with a low content of U^{234} , uranium was leached out by natural waters, whereas the samples high in U^{234} were enriched in this isotope by secondary processes of different kinds.

In such manner, the analysis of our experimental findings is sufficient only as a basis for certain preliminary considerations regarding the isotopic composition of uranium in natural materials. However, the direct method of determination of the isotopic composition of uranium, as employed by us, makes it possible to determine the U^{234}/U^{238} ratio with a high degree of reliability and suggests further possibilities in its extensive applications in problems of the origins and behavior of uranium in natural materials of different kinds.

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THE FUNDAMENTAL STAGES OF HYDROTHERMAL ACTIVITY OF KAMCHATKA AND KURILE ISLANDS VOLCANOES AND THE ASSOCIATED TYPES OF THERMAL WATERS

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Abstract

The division of volcanic gases into two chief groups—the “fumarolic” gas and the “solfataric” gases is to a great extent conditioned by their interaction with underground waters. In the ranges of the volcanic zone of the Kuril islands—Kamtchatka, four stages of hydrothermal action of volcanoes and three chief genetic types of thermal waters are distinguished—acid sulfate, acid sulfate-chloride and alkaline chloride waters, the composition of which is shown in the tables.

Regions of active modern volcanism, particularly the Kamchatka and the Kuriles, are distinguished by many characteristic hydrochemical relationships and processes which are not observed in other geological and hydrochemical environments, as indicated by an extensive body of data accumulated in recent decades. These characteristics, determined by the presence of high-temperature volcanic gases and by the exceptionally high geothermal regime, are expressed in a powerful and distinct modern hydrothermal activity, in the formation of thermal waters of unusual composition, and in the development of a peculiar vertical geochemical zoning in regions of active volcanic centers.

1. INTERACTIONS OF VOLCANIC GASES, VAPORS, AND UNDERGROUND WATERS

The composition of volcanic gases and vapors discharging at the surface is determined not only by the character and activity of abyssal volcanic hearths and by the thermodynamic environments in the depths, but also to a major extent by geothermal and hydrologic environments at shallow depths, as is shown by the now available data [7, 8, 9].

All of the gas-vapor streams discharging within the areas of present volcanism may be divided into four principal groups on the basis of the environments of their origin, composition, and temperature (Table 1).

The high-temperature volcanic gases of a very complex composition and containing different proportions of individual constituents (HCl , H_2S , SO_2 , CO , CO_2 , and many others), containing also up to 90% water

Table 1. Principal Types of Gaseous-Vapor Exhalations in Areas of Active Volcanoes

Type of exhalation	Temperature at surface, °C	Preponderant constituents, at surface	Origin
Volcanic Gases			
1. High-temperature (chlorine-sulfur-carbon dioxide)	Hundreds	H ₂ O; HCl; H ₂ S; SO ₂ ; CO; CO ₂ ; N ₂ (with rare gases); O ₂ ; occasionally NH ₃ ; CH ₄ ; others	Magmatic and thermometa-morphic gases (secretions of magmatic hearths and of strongly heated rocks); partially modified by interactions with gases of atmospheric origin
2. Low-temperature (hydrogen sulfide-carbon dioxide)	100 to 150	CO ₂ ; H ₂ S; H ₂ O; occasionally CH ₄	Magmatic and thermometa-morphic gases filtered through underground waters
I. Water vapor			
1. Abyssal	About 100	H ₂ O; traces of CO ₂ ; N ₂ (with rare gases); traces of H ₂ S; occasionally CH ₄	Conversion into steam ("underground boiling") of abyssal superheated waters under pressure
2. Surficial	About 100	H ₂ O; (traces of rare gases); O ₂ ; traces of CO ₂	Conversion of descending cold waters into steam in hot rocks

vapor as their principal constituent, are able to reach the surface (as a rule, through craters of active volcanoes) only in extremely high geothermal environments, precluding the possibility of existence of the underground waters in their liquid state and of the absorption of the ascending abyssal volcanic gases and vapors by the waters.

A part of these high-temperature volcanic gases is evidently of an abyssal (magmatic) origin, whereas another part appears to be forming in the upper zones of the gas-conducting channels, by interaction between the abyssal gases and oxygen of the air. As the result, nitrogen too makes its appearance in large quantities in the gases of such origin.

In the lower-temperature geothermal environments, where the ascending streams of volcanic gas-vapor meet with underground waters, at this or that depth, they become partially dissolved in these waters, so that only some of them are able to reach the surface: chiefly CO₂, H₂S, N₂, and, on occasions, CH₄. Water vapor will reappear in such

gases, in appreciable quantities, only if the gases had passed through horizons of very hot waters before their emergence at the surface.

In such manner, it is the geothermal and the associated hydrologic environments that are responsible, first of all, in our opinion, for the two clearly defined principal categories of the gases: the chlorine-sulfur-carbon dioxide group and the hydrogen sulfide-carbon dioxide group. These groups are called the "fumarole" and the "solfataric" group respectively in volcanologic literature.

Discharges of steam containing insignificant admixtures of the gases are also fairly extensive, in areas of modern volcanism, as the result of a conversion of the very hot underground waters into vapor. The most important ones are the emanations of steam from highly thermal (extremely superheated) waters under pressure which ascend hydrostatically to the near-surface zones.

In this case, as was shown by K. P. Florenskii's most recent studies*, the gases dissolved in underground waters, specifically, N_2 , CO and H_2S , are expelled almost quantitatively, together with the steam, in the course of such ascension. In the course of this process, hydrogen sulfide may acquire a high geochemical significance, despite its small concentrations in the ground waters, as it causes the formation of ferrous sulfide in ferruginous rocks (in reducing environments) and of strongly acid sulfate solutions in the surficial (strongly oxidizing) environments resulting in intensive decomposition of the rocks.

If the emanation of steam from strongly superheated waters become quantitatively important, such waters become subject to changes in their composition: they lose practically all of the dissolved gases and their content of dissolved salts increases appreciably.

2. FUNDAMENTAL STAGES OF HYDROTHERMAL ACTIVITY OF VOLCANOES

Modern geochemical activity of volcanoes is expressed in many different ways: in emanations of volcanic gases and vapors of different composition and temperature, in formation of acid and alkaline waters of different kinds, in decomposition of rocks, both by vapors and by waters, and by leaching out of metals, silica, and other constituents from the rocks. It is entirely evident that the character of hydrothermal activity of volcanoes changes substantially with the evolution of the volcanic hearths and of the gradual cooling of the gas-conducting channels. The available data for the Kamchatka and the Kuriles allow us to distinguish four principal types or stages of the volcanic hydrothermal activity.

Stage I is characterized by the maximum of the hydrothermal activity, by severe super-heating (up to hundreds of degrees C.) of the

*Report at the Conference, the Pauzhet Geothermal Station of the Laboratory of Volcanology, Academy of Sciences of the USSR, Kamchatka, September, 1957.

por-conducting channels and fissures throughout their extent from the depths to the surface of the earth. Temperatures of the emerging gases are considerably above 100°C . The emerging gases have a complex composition. Their characteristic constituents (preponderant quantitatively, as a rule), not considering steam and gases of atmospheric origin, are HCl , HF , CO , CO_2 , H_2S , SO_2 , generally B, and certain others.

The gases of the Klyuchevskaya Sopka and of the Sheveluch Volcanos, in Kamchatka, and of the East Ebeko* and of some others, in the Kuriles (Table 2), may be regarded as examples, in this connection.

Strongly acid chloride or chloride-sulfate thermal waters are the results of a partial entry of the gases here enumerated into surficial reservoirs of waters as well as into underground waters.

Stage II. The upper parts of the gas-conducting channels are cooled off to a considerable degree. The ascending abyssal vapors are condensed accordingly and serve to enrich the underground waters they may encounter, with resulting complete removal of HCl , HF , B, SO_2 , and certain other constituents from the gas. The remaining gas is chiefly CO_2 , H_2S , as well as N_2 (and the rare gases) and, occasionally, H_4 , that are able to reach the surface, as they pass through the more or less hot underground waters, where they emerge as the characteristic streams of hydrogen sulfide-carbon dioxide (Table 2).

In this stage, there is a formation of two characteristic types of waters in the volcanic massifs: the sulfate-chloride waters (analogous to the thermal waters of Stage 1) in the lower horizons and of entirely sulfate waters in the levels not far below the surface.

Stage III is characterized by an appreciable diminution of hydrothermal activity and by a cooling of the rocks of which the volcanic massifs are composed. The gases discharging at the surface are of the hydrogen sulfide-carbon dioxide type, as in Stage II, at about 100°C . The gas discharge yields thermal waters only of the acid sulfate type. There is no formation of chloride-sulfate thermal waters (unlike Stages I and II), which may be due either to a complete absorption of the high-temperature chlorine-bearing gases by underground waters at great depths or to a cessation of the evolution of such gases in the magmatic hearth itself.

Stage IV is characterized by a complete (or nearly complete) cessation of the evolution of volcanic gases. Only steam, derived from strongly heated underground waters, makes its appearance at the surface. The gaseous solutes of the original thermal waters are reflected directly in the small amounts of gases carried by the steam: CO_2 , H_2 , (and the rare gases), traces of H_2S , and, occasionally, CH_4 . If such streams of steam chance to penetrate some small stagnant bodies of surface waters or waters of the soil or of the ground (also, if their gaseous constituents include even minute traces of H_2S), there follows

Table 2. Composition of Some Typical Volcanic Gases in Kamchatka and in Kurile Islands

Source of gas	Date of collection	Temperature of gas, °C.	Per cent by volume										Remarks**	
			HCl	HF	H ₂ S	SO ₂	CO	CO ₂	CH ₄	H ₂	NH ₃	O ₂		N ₂ and rare gases
I. High Temperature Gases (corrected for air and water vapor)														
Kamchatka	May-Aug., '49	340 to 500 240 to 490	3.20	0.15	-	0.75	3.94	-	-	5.07	-	-	86.53	Av. of 4 analyses
			1.12	-	-	7.16	2.03	-	-	4.29	-	-	85.40	Av. of 6 analyses
	Nov.-Dec., '53	180 to 295 110 to 280	13.99	present	-	3.03	6.71	9.73	-	3.06	-	-	63.48	Av. of 3 analyses
			1.47	present	-	27.11	2.76	48.25	-	4.50	-	-	15.90	Av. of 2 analyses
II. Low Temperature Gases														
Kamchatka	Sept., '55	48.0	-	-	0.82	-	-	90.62	5.51	-	-	-	21.20	
			-	-	15.93	-	-	81.75	0.12	-	-	-	2.20	
	Sept., '54	43.0	-	-	-	-	-	-	-	-	-	-	-	
			-	-	-	-	-	-	-	-	-	-	-	-
Kunashir Island	Oct., '54	69.0	-	-	16.20	-	-	82.30	0.10	-	-	-	1.40	
			-	-	48.40	-	-	48.20	1.22	-	-	-	3.94	
	Sept., '54	91.3	-	-	present	-	-	10.82	-	-	-	-	89.18	
			-	-	-	-	-	-	-	-	-	-	-	-

*Collected and analyzed by L. A. Basharina [1,2].

†Collected by V. V. Ivanov; analyzed by I. S. Krasnikova.

**Averages and corrections for air and water vapor, in some samples, calculated by the author.

development of weakly acid and generally weakly mineralized waters of the sulfate-bicarbonate type, resembling the previously described thermal sulfate waters. The emergence of the steam, in some instances, is accompanied by the discharge of the thermal waters themselves.

Among typical examples of such hydrothermal activity we may cite the Pauzhet Springs in the Kambalny Range in southern Kamchatka, the Geiser Valley in eastern Kamchatka, the Cape Dokuchev area of Kunashir Island and several other places in the Kuriles-Kamchatka volcanic zone.

3. THE PRINCIPAL TYPES OF THERMAL WATERS IN REGIONS OF ACTIVE VOLCANIC HEARTHS

It is evident from the foregoing considerations that the formation of thermal waters of different types in regions of active volcanism is determined, first, by the composition of volcanic gases and, second, by the thermal regime inside the volcanic masses. As it has been already stated, we may distinguish three main types of thermal waters in regions of active volcanic hearths.

I. Acid Sulfate Therms

Acid sulfate thermal waters forming in surficial horizons of volcanic rocks, in strongly oxidizing environments effective only within the areas of discharging volcanic gases, are chiefly ground waters and, in places, surface waters saturated by volcanic gases that had already been filtered, in depths, by underground waters.

The gases evolving from such waters, commonly in appreciable quantities, at temperatures of 60 to 100°C, consist almost entirely of CO_2 and H_2S (not counting water vapor), rarely with small admixtures of CH_4 and N_2 . Moreover, their H_2S content generally does not exceed 15 to 20% of the total volume but may be 45 to 50% in exceptional cases. However the H_2S content of the waters themselves, at relatively low temperatures, may be very high (e.g. 300 milligrams/liter).

Characteristically, chlorides are nearly absent among the anions, whereas the cations include constituents of many different kinds; H, Ca, Mg, Fe, Al, and, in places, NH_4 .

All waters of this type are distinguished by their high acidity (ph 5.5 to 1, as a rule), which is due to the presence of free H_2SO_4 , and by their wide range of variation in the dissolved salts (1 to 7.5 grams/liter) which depends in many respects on the relative abundance of water and on the discharge of the springs themselves (Table 3).

The acid sulfate thermal waters here discussed are called by us the "*fumarole therms of surficial origin*" [7], so extensively distributed on many active volcanoes of Kamchatka (Verkhne-Semyachinsk Springs, Zapovednye, Verkhne- and Nizhne-Koshelevskie Springs, and others), as well as in the Kuriles (Mendelevskie, Golovninskie,

Table 3. Acid Sulfate Thermal Waters

Source, date, temperature, and discharge*	Kamchatka, Uzonskie (Chernyi Istochnik)† ("Black Spring"); Sept. 25, 1951; insignificant discharge			Iturup Island, Sernozavodskii Istochnik** (Sulfur Plant Spring); Sept. 15, 1951; tem. of water: 43°C; discharge: 4 liters/sec			Kunashir Island, Mendeleevskii-Severnii ("Mendeleev-Northern"); Thermal waters†; Kislyi Ruchei (Acid Brook), Sept. 23, 1953; temp. of water: 67.0°C; discharge: insignif.		
	grams/liter	m.e./liter	m.e.-%	grams/liter	m.e./liter	m.e.-%	grams/liter	m.e./liter	m.e.-%
Cations									
H ⁺	0.0056	5.60	15.45	0.0088	8.81	22.64	0.0200	0.0339	33.90
Li ⁺	-	-	-	-	-	-	-	-	-
NH ₄ ⁺	0.3149	17.44	48.15	not detected	-	-	0.0080	0.0001	-
Na ⁺	0.0270	1.20	3.31	0.0121	0.53	1.36	0.4551	0.1176	5.11
K ⁺	0.0118	0.28	0.79	0.0051	0.13	0.33	0.0096	0.0008	0.02
Mg ²⁺	0.0054	0.44	1.21	0.0091	0.75	1.92	0.0087	0.0414	3.40
Ca ²⁺	0.0112	0.56	1.54	0.1950	9.72	24.98	0.0791	0.0800	4.00
Sr ²⁺	-	-	-	0.0007	-	-	trace	0.0018	0.04
Ba ²⁺	-	-	-	not detected	-	-	not detected	-	-
Fe ²⁺	0.0009	0.05	0.13	not detected	-	-	0.1124	0.1232	4.40
Fe ³⁺	0.1699	9.09	25.09	not detected	-	-	0.0344	0.0336	1.86
Al ³⁺	0.0132	1.46	4.03	0.1707	18.97	48.77	0.0779	0.2278	25.31
Mn ²⁺	0.0028	0.10	0.28	-	-	-	0.0006	0.0010	0.03
Cu ²⁺	not detected	-	-	-	-	-	0.0003	0.0009	0.04
Ti ⁴⁺	0.0004	0.01	0.02	-	-	-	0.00035	0.00003	0.07
Sum of cations	0.5631	36.23	100.00	0.4015	38.91	100.00	0.8061	0.6621	78.14
Anions									
F ⁻	0.0004	0.02	-	0.0012	0.06	0.15	0.0009	0.0016	0.08
Cl ⁻	0.0130	0.38	1.05	0.0380	1.07	2.75	0.0925	0.0063	0.18
Br ⁻	0.0001	-	-	not detected	-	-	0.0004	not detected	-
I ⁻	not detected	-	-	not detected	-	-	not detected	-	-
SO ₄ ²⁻	1.7216	35.83	98.95	1.5657	32.62	83.83	2.0190	2.2387	46.64
HSO ₄ ⁻	-	-	-	0.5005	5.16	13.27	1.5910	3.0303	31.24
HPO ₄ ⁻	not detected	-	-	-	-	-	-	0.0008	-
Sum of anions	1.7351	36.25	100.00	2.1054	38.91	100.00	3.7038	5.2777	78.14
Undissoc. molecules									
H ₂ SiO ₃	0.2420	-	-	0.1534	-	-	0.3568	0.4098	-
H ₃ AsO ₃	not detected	-	-	0.0009	-	-	0.0011	not detected	-
HBO ₂	not detected	-	-	-	-	-	0.0490	not detected	-
H ₂ S	-	-	-	0.3009	-	-	0.0442	-	-
Total mineralization}	2.5402	-	-	2.6824	-	-	4.9610	6.3496	-
pH	2.3	-	-	2.02	-	-	1.70	1.47	-

*Water samples of springs were collected by the author.

†S. S. Kravtchina, Analyst

**E. F. Prokof'eva, Analyst

Sernozavodskie, and many others). Such waters are well represented also in other areas of modern active volcanism: Iceland, Italy, Japan, and elsewhere.

II. Acid Chloride or Sulfate-Chloride Therms

This type of water is formed in high-temperature environments, as the result of saturation of underground waters by chloride-sulfate-carbon dioxide volcanic gases. Appreciable quantities of free sulfuric acid and, in places, free hydrochloric acid are present and the waters are strongly acid accordingly, with pH on the acid side of 3, as a rule, and even on the acid side of pH1.

The cations are complex, including different proportions of H, Al, Fe, Na, and Ca, depending on interactions between the acid waters and the young volcanic rocks. This type of thermal water is distinguished by high concentrations of dissolved silicic acid (H_2SiO_3), Fe, and Al, and also by generally high concentrations of boron.

The total mineralization of these waters, here called the "*fumarole therms of deep origin*" is not over 5 grams per liter, as a rule, although it may be considerably higher, on occasions, as in the Verkhne-Yur'evskii Spring (17 grams/liter, Table 4).

The unusually high Cl/Br ratios (commonly higher than 2000 to 3000) are definitely characteristic of such waters (Table 5).

There is very little dissolved gas in waters of this type when they emerge at the surface, from fissures in volcanic rocks at some distance from the gas-conducting channels. It appears that gases are almost completely expelled from these high-temperature waters before they have a chance to come to the surface.

At the surface the waters are very hot, as a rule practically at the boiling point in many places, and their discharge is indeed considerable: up to tens of liters per second (Golovninskoe Ozero, Kunashir Island; Yur'evskie Springs, Paramushir Island). Waters of the type here discussed are found only in the Kurile Islands, in the USSR; none was found so far in Kamchatka.

Their many analogues may be found among the therms of Japanese volcanoes (the Moto-Yu Spring, "Shibukuro") and also in some crater lakes (such as in Indonesia, etc.), and in waters forming from precipitation on fresh volcanic ash.

III. Alkaline Chloride Therms

The alkaline chloride type of thermal water originates in the zones of thermal action of the volcanic hearths, in high-temperature strongly reducing environments, generally at appreciable depths, both in the well-leached bodies of marine and volcanogenic sediments and in the volcanic rocks.

Such waters are highly superheated in the depths (up to 200 to 300°C, and higher) and they emerge at the surface generally at high pressures, boiling and steaming, along major zones of tectonic fracturing, as they

Table 4. Acid Sulfate - Chloride Thermal Waters

Source, date, temperature of water, and discharge*	Kunashir Island, Kislyi Kiyuch ("Acid Spring"), Istochnik Osnovnoi ("Main Flow"),† Sept. 15, 1953; 55.6°C; 2.8 liters/sec				Kunashir Island; Nizhne-Mendelevskie Kiyuchi ("The Lower Mendelev Springs") Istochnik Osnovnoi ("Main Flow"),† Oct. 30, 1954; 91.3°C; 7.0 liters/sec				Kunashir Island; Golovinskoe Hot Lake; discharge from lake,** Sept. 23, 1953; 30.0°C; more than 50 liters/sec	
	grams/liter	milliequiv/liter	milliequiv, %		grams/liter	milliequiv/liter	milliequiv, %		grams/liter	milliequiv/liter
Cations										
H ⁺	0.0040	3.99	6.43		0.0200	20.00	32.85		0.0031	3.16
NH ₄ ⁺	0.0001	-	-		0.0069	0.38	0.62		not detected	-
Na ⁺	0.3171	13.79	23.94		0.1212	5.27	9.59		0.3279	14.26
K ⁺	0.0463	1.18	1.90		0.1047	2.67	3.37		0.0206	0.52
Mg ²⁺	0.0788	6.41	10.28		0.0680	5.64	8.99		0.0349	1.81
Ca ²⁺	0.1640	8.20	13.26		0.1496	7.43	12.10		0.1242	2.87
Str ²⁺	0.0030	0.06	0.09		0.0009	-	-		-	6.20
Ba ²⁺	not detected	-	-		not detected	-	-		-	-
Fe ²⁺	0.0560	2.00	3.21		0.2194	7.84	12.80		0.0113	0.60
Fe ³⁺	0.1008	8.40	13.43		0.0312	1.68	2.74		0.0050	0.17
Al ³⁺	0.1369	17.11	27.43		0.0930	10.35	16.94		0.0080	0.39
Mn ²⁺	0.0002	-	-		0.0004	-	-		0.0024	0.08
Ti ⁴⁺	0.0003	0.02	0.03		0.0002	-	-		-	-
Cu ²⁺	0.00004	-	-		0.00009	-	-		-	-
Sum	0.9075	61.16	100.00		0.81559	61.26	100.00		0.5374	28.75
Anions										
F ⁻	0.0008	0.04	0.06		0.0012	0.06	0.09		-	-
Cl ⁻	1.4392	40.58	65.58		0.9825	27.77	45.33		-	-
Br ⁻	0.0007	-	-		0.0003	-	-		0.8442	23.81
I ⁻	not detected	-	-		not detected	-	-		not detected	-
SO ₄ ²⁻	0.9312	19.40	31.00		1.1539	24.04	39.30		not detected	-
SO ₃ ²⁻	0.1106	1.14	3.86		0.9108	9.39	15.38		0.2237	4.66
HPO ₄ ²⁻	0.0001	-	-		-	-	-		0.0271	0.28
NO ₃ ⁻	not detected	-	-		-	-	-		0.0009	-
NO ₂ ⁻	not detected	-	-		-	-	-		-	-
HCO ₃ ⁻	not detected	-	-		-	-	-		-	-
CO ₃ ²⁻	not detected	-	-		-	-	-		-	-
Sum	2.4826	61.16	100.00		3.0487	61.26	100.00		1.0958	28.75
Undissociated molecules										
H ₂ SiO ₃	0.4260	-	-		0.3515	-	-		0.1183	-
H ₂ AsO ₃	0.0008	-	-		0.0015	-	-		not detected	-
HBO ₃	0.1239	-	-		0.1307	-	-		-	-
Total mineralization	3.9408	-	-		4.3479	-	-		1.7516	-
pH	2.4	-	-		1.7	-	-		2.5	-

*Spring waters sampled by the author; †S. S. Krasnitskii; **A. A. Ivanov

Table 5. Summary of Characteristics of Chemical Composition of Some Typical Acid Thermal Waters of Kamchatka and Kurile Islands

Item	Name of springs	Temp. of water, °C	Total mineralization grams/liter	Formula of chemical composition	HCl, g./l.	H ₂ SO ₄ g./l.	H ₂ SiO ₃ mg./l.	HBO ₂ mg./l.	pH	Cl/Br
I. Sulfate Therms										
1	Uzonkie; Kamchatka; Chernyi Istochnik ("Black Spring")	-	2.5	$\frac{(\text{SO}_4 + \text{HSO}_4)_{99}}{\text{NH}_4^{43}\text{Fe}_{23}\text{H}_{17}}$	-	-	242.0	not detected	2.3	-
2	Verkhne-Semyachinakie; Iturup Island	96.2	1.0	$\frac{\text{SO}_4^{16}}{\text{NH}_4^{18}}$	-	-	80.0	-	6.2	-
3	Sernozavodskii; Iturup Island	43.0	2.7	$\frac{(\text{SO}_4 + \text{HSO}_4)_{97}}{\text{Al}_9\text{Ca}_{23}\text{H}_{23}}$	-	-	153.4	21.3	2.2	-
4	Mendeleevskie Severnye; Kunashir Island	69.0	4.9	$\frac{(\text{SO}_4 + \text{HSO}_4)_{98}}{\text{H}_{33}(\text{Na} + \text{K})_{33}\text{Al}_{14}\text{Fe}_{12}}$	-	-	356.8	49.0	1.7	-
II. Sulfate-Chloride and Chloride Therms										
1	Nizhne-Mendeleevskie; Kunashir Island	91.3	4.3	$\frac{(\text{SO}_4 + \text{H}_2\text{SO}_4)_{55}\text{Cl}_{45}}{\text{H}_{32}\text{Al}_{17}\text{Fe}_{26}}$	-	-	351.5	130.7	1.7	3275
2	Kislyi Klyuch; Kunashir Island	55.6	3.9	$\frac{\text{Cl}_{69}(\text{SO}_4^{44} + \text{H}_2\text{SO}_4^{34})}{\text{Al}_{28}(\text{Na} - \text{K})_{26}\text{Fe}_{17}}$	-	-	426.0	123.9	2.4	2056
3	Verkhne - Yur'evskii; Paramushir Island	95.0	17.6	$\frac{\text{SO}_4^{17}\text{Cl}_{45}}{\text{H}_{44}\text{Al}_{21}}$	5.2	0.55	317.0	high	0.86	9600
4	Central Funnel of the Upper Crater, Ebeko Volcano; Paramushir Island	100.0	66.8	$\frac{\text{Cl}_{69}}{\text{H}_{88}}$	64.8	-	76.8	very high	-1.70	1403

develop into groups of springs or in places into geysers of high discharge (up to tens of liters per second).

It is these particular waters, out of all other known types of therms that are the hottest ones. They are carriers of great quantities of thermal energy and are therefore subjects of some interest in this connection.

Their characteristic and uniform composition in the entire area of the Kuriles-Kamchatka modern active volcanism is determined by the specific environment of their origin. These therms are of the sodium chloride type and they contain only small admixtures of sulfates (not over 100 to 120 mg/l as a rule) together with conspicuously high boron, high silicic acid, and a strongly alkaline reaction (pH 8.0 to 8.7, Table 6).

The total mineralization of these waters is generally 2 to 5 grams per liter. However, the original mineralization of these waters must be somewhat lower in depths, inasmuch as there must be an increase in the concentration of their solutes in surficial environments because of appreciable loss of their solvent (water) as steam. The chlorine/bromine ratio in these waters is generally higher than it is in the sea (up to 500-700).

The gaseous constituents of these therms, according to the most recent studies of their condensates (K. P. Florenskii) must be regarded as of the nitrogen-carbon dioxide type (occasionally with a small admixture of H_2S); their total gas content is apparently insignificant. As to their origin, these waters are chiefly atmospheric-infiltrational.

It is entirely evident also that a certain fraction of the chlorine dissolved in these waters is derived from volcanic rocks and that, in such typically volcanic regions as Iceland, all their chlorine comes from volcanic rocks.

The extremely low sulfate content, against the background of high-sulfate ground waters of volcanic areas, is their characteristic feature. One is led to believe that the dissolved sulfates prove to be unstable in the high-temperature strongly reducing environments and are decomposed for that reason, while their oxygen is expended in oxidation processes of different kinds [3].

An even more characteristic example of this type of water are the superheated waters explored in recent years in the Wairakei District, New Zealand, by special drilling for sources of energy, as well as in Iceland, in the Krisuvik District visited by the author in 1957 (Table 7).

PRINCIPAL CONCLUSIONS

1. The character and intensity of hydrothermal activity of modern volcanoes are determined not only by activities of abyssal volcanic hearths, but, and by no means to a lesser degree, by thermodynamic and hydrologic environments operative in the upper horizons of volcanic bodies.

Source, date, temperature of water, and discharge	Pauzhet; Kamchatka (Istochnik Paryashchii No. 1)† ("Steam Spring"); Oct. 18, 1950; 100°C; 10.2 liters/sec						Geizerye Springs (Geizer Velikan)** ("Geyser Giant"); Kamchatka; Sept. 27, 1951; 98.9°C; 1.4 liters/sec						Goryachii Pivazh ("Hot Strand") (Istochnik Glavnyi)** ("Main Spring"); Kamashir Island; Sept. 25, 1954; 100°C; 0.3 liters/sec					
	grams/liter	milliequiv/liter	milliequiv.-%	grams/liter	milliequiv/liter	milliequiv.-%	grams/liter	milliequiv/liter	milliequiv.-%	grams/liter	milliequiv/liter	milliequiv.-%	grams/liter	milliequiv/liter	milliequiv.-%	grams/liter	milliequiv/liter	milliequiv.-%
Cations																		
NH ₄ ⁺	-	-	-	-	-	-	not detected	-	-	-	-	-	0.0003	0.01	-	0.0003	0.01	0.01
K ⁺	0.0881	2.25	4.46	-	1.53	5.24	0.0599	1.53	5.24	-	1.53	5.24	0.2430	6.20	-	0.2430	6.20	8.97
Na ⁺	1.0100	44.36	87.56	-	25.98	89.18	0.5972	25.98	89.18	-	25.98	89.18	1.3388	58.21	-	1.3388	58.21	84.28
Mg ²⁺	0.0101	0.41	1.64	-	0.30	1.02	0.0037	0.30	1.02	-	0.30	1.02	0.0050	0.41	-	0.0050	0.41	0.58
Ca ²⁺	0.0641	3.30	6.34	-	1.33	4.56	0.0266	1.33	4.56	-	1.33	4.56	0.0846	4.23	-	0.0846	4.23	6.16
Si ³⁺	-	-	-	-	-	-	-	-	-	-	-	-	0.0012	-	-	0.0012	-	-
Ba ²⁺	-	-	-	-	-	-	-	-	-	-	-	-	not detected	-	-	not detected	-	-
Fe ²⁺	not detected	-	-	-	-	-	not detected	-	-	-	-	-	not detected	-	-	not detected	-	-
Fe ³⁺	not detected	-	-	-	-	-	-	-	-	-	-	-	not detected	-	-	not detected	-	-
Al ³⁺	not detected	-	-	-	-	-	-	-	-	-	-	-	not detected	-	-	not detected	-	-
Mn ²⁺	-	-	-	-	-	-	not detected	-	-	-	-	-	not detected	-	-	not detected	-	-
Cu ²⁺	-	-	-	-	-	-	not detected	-	-	-	-	-	not detected	-	-	not detected	-	-
Ti ⁴⁺	-	-	-	-	-	-	-	-	-	-	-	-	0.00006	-	-	0.00006	-	-
Sum	1.1723	50.22	100.00	-	29.14	100.00	0.8574	29.14	100.00	-	29.14	100.00	1.6730	69.06	-	1.6730	69.06	100.00
Anions																		
F ⁻	0.0008	0.04	0.07	-	-	-	-	-	-	-	-	-	0.0009	0.04	-	0.0009	0.04	0.06
Cl ⁻	1.6840	47.52	44.12	-	24.26	83.27	0.8588	24.26	83.27	-	24.26	83.27	2.3545	66.40	-	2.3545	66.40	90.16
Br ⁻	0.0032	0.03	0.06	-	0.01	0.03	0.0013	0.01	0.03	-	0.01	0.03	0.0034	0.04	-	0.0034	0.04	0.06
I ⁻	not detected	-	-	-	-	-	not detected	-	-	-	-	-	0.0002	-	-	0.0002	-	-
SO ₄ ²⁻	0.0831	1.73	3.42	-	2.36	8.09	0.1135	2.36	8.09	-	2.36	8.09	0.0542	1.13	-	0.0542	1.13	1.63
HCO ₃ ⁻	0.0366	0.60	1.19	-	1.33	4.57	0.0810	1.33	4.57	-	1.33	4.57	0.0884	1.45	-	0.0884	1.45	2.09
CO ₃ ²⁻	0.0090	0.30	0.60	-	1.28	4.04	0.0384	1.28	4.04	-	1.28	4.04	not detected	-	-	not detected	-	-
NO ₂ ⁻	not detected	-	-	-	-	-	not detected	-	-	-	-	-	not detected	-	-	not detected	-	-
NO ₃ ⁻	not detected	-	-	-	-	-	not detected	-	-	-	-	-	not detected	-	-	not detected	-	-
Sum	1.8167	50.22	100.00	-	29.14	100.00	1.0930	29.14	100.00	-	29.14	100.00	2.5016	69.06	-	2.5016	69.06	100.00
Undissociated molecules																		
H ₂ SiO ₃	0.2100	-	-	-	-	-	0.3325	-	-	-	-	-	0.3094	-	-	0.3094	-	-
H ₃ AsO ₃	0.0018	-	-	-	-	-	0.0002	-	-	-	-	-	0.0008	-	-	0.0008	-	-
HBO ₂	0.1580	-	-	-	-	-	0.0841	-	-	-	-	-	0.1048	-	-	0.1048	-	-
Total mineralization	3.3588	-	-	-	-	-	2.3672	-	-	-	-	-	4.5896	-	-	4.5896	-	-
pH	8.4	-	-	-	-	-	8.7	-	-	-	-	-	8.1	-	-	8.1	-	-

*Samples of waters from springs collected by the author.

†E. F. Prokof'eva, Analyst. H₂SiO₃ and HBO₂ determined in 1957 by S. S. Krapivina.

**S. S. Krapivina, Analyst.

Table 7. Brief Comparative Characteristics of Chemical Composition of Alkaline Chloride Therms of Kamchatka and Kurile Islands and of Some of their Analogues

Item	Name of springs	Temp. of water °C	Total mineralization grams/liter	Formula of chemical composition	H ₂ SiO ₃ , mg, liter	HBO ₂ , mg, liter	pH	Cl Br	$\frac{rNa + rK}{rCl}$
1	Kamchatka; Geizer Velikan Dolina Geizerov ("Geyser 'Giant', the Valley of Geysers")	98.9	2.4	$\frac{Cl_{83}}{(Na+K)_{94}}$	0.332	84.1	8.7	337 av.	1.13
2	Kamchatka; Pauzhet Springs	100.0	3.4	$\frac{Cl_{83}}{(Na+K)_{92}}$	0.249	125.0	8.4	530	0.98
3	Kunashir Island; Goryachii	100.0	4.6	$\frac{Cl_{96}}{(Na+K)_{93}}$	0.309	104.8	8.1	735 av.	0.98
4	New Zealand; Wairakei District (Borehole No. 4)*	100.0	3.9	$\frac{Cl_{97}}{(Na+K)_{95}}$	0.502	106.0	8.6	—	0.97
5	Iceland; Krizuvik District†	100.0	2.2	$\frac{Cl_{87}}{(Na+K)}$	0.648	Not detected	9.1	425	1.06

*According to S. H. Wilson [17].

†Analysis by S. S. Krapivina and E. P. Ryabichkina; samples collected by the author in 1957.

2. The common classification of volcanic gases into two major groups, the so-called "fumarole" and "sulfataric" gases, is well sustained by the differences in the hydrologic-geothermal environment in which these gases emerge at the surface.

The fumarole gases are high-temperature volcanic exhalations which did not pass through underground waters.

The solfataric gases are the relatively low-temperature "residual" volcanic gases which were "filtered through" underground waters.

3. The following four stages of hydrothermal volcanic activity may be distinguished within the boundaries of the Kuriles-Kamchatka zone:

Stage I is characterized by great exhalations of very hot chlorine-sulfur-carbon dioxide gases and by the formation of strongly acid thermal waters containing free sulfuric and hydrochloric acids.

Stage II is characterized by emergence at the surface of only low-temperature hydrogen sulfide-carbon dioxide gases and by the formation of acid sulfate thermal waters in the surficial zones; chloride-sulfate thermal waters are formed in the deeper horizons, under the influence of the chlorine-sulfur-carbon dioxide gases.

Stage III is distinguished by the presence of only hydrogen sulfide-carbon dioxide gaseous emanations and by the formation of the acid sulfate waters only.

Stage IV is distinguished by the presence only of steam flows (with small admixtures of certain gases) due to the evaporation of strongly superheated underground waters.

4. In regions subjected to thermal effects of active volcanic hearths in abyssal high-temperature reducing environments, there is a formation of strongly superheated alkaline sodium chloride thermal waters

generally weakly mineralized, low in dissolved gases (CO_2 and N_2 are the principal constituents), and markedly high in boron and H_2SiO_3 .

5. The abyssal superheated chloride therms of active volcanic regions carry a particularly large amount of heat and are particularly important for that reason as sources of energy. Such therms are utilized in Italy and New Zealand for the production of electric energy.

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THE CHEMICAL COMPOSITION OF ISOMETRIC
TITANIUM-TANTALUM NIOBATES

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Abstract

The empirical formulas of minerals differ markedly from the theoretical formulas universally adopted for them. A deficiency of cations in the "A" group has been ascertained. In connection with this the formula $A_{n-x}B_pX_q$ is proposed, where x is the value determining the deficiency in the atomic amounts of the "A" group.

The atomic amounts of the cations of the group "A" in the cubic titanium-tantalum niobates range from 2.0 to 0.5, a definite dependence between the size of the cation deficiency in the group "A" and the content of titanium, zirconium, uranium, thorium and water in minerals having been observed. The usual minerals with an increased cation deficiency in the "A" group are metamict minerals.

Results of x-ray investigations of the isometric titanium-tantalum-niobates are given in the paper and the dependence of the size of the elementary mineral cell on the titanium content has been established. On the basis of the ascertained regularities in the composition and structure of the isometric titanium-tantalum-niobates a rational classification of minerals belonging to this group has been proposed.

Minerals grouped together under the collective name of titanium-tantalum niobates have been subjects of interest for many investigators for a long time. Indeed, they are regarded as one of the most complex groups in mineralogy. Despite the fact that an appreciable number of titanium-tantalum niobates have been studied repeatedly by many investigators, many of their aspects still remain obscure, particularly some problems pertinent to their chemical composition. For example, a detailed classification of these minerals had not been developed, even up to now, that would take into account all of the characteristics of their structures and composition: chemical formulas proposed for many of the minerals do not represent their chemical composition; even now, there are no criteria for the identification of mineral species and their varieties, among the titanium-tantalum niobates; there are no reliable and rapid methods for their diagnosis.

The minerals here discussed have the following specific characteristics:

1. Alongside the crystalline minerals, among titanium-tantalum niobates, their metamict varieties containing, as a rule, the rare earths, uranium, and thorium [1, 11] are very common.

2. Titanium-tantalum niobates are distinguished by their highly complex and generally variable chemical composition. Their principal constituents are: Nb, Ti, Ta, Fe, Mn, Ca, Na, U, Th, the rare earths. The less common ones, present in subordinate quantities, are: K, Mg, Al, Ba, Sr, Pb, Sn, Sb, Bi, Zn, Si, P; also H_2O and F are commonly present (the pyrochlore-microlite group). Such complexity of the chemical composition may be ascribed to several causes: the wide incidence of both isovalent (Nb-Ta, Fe-Mn-Mg, Ca-Sr-Ba) and heterovalent (Nb-Ti, Ca-Na-rare earths-U, Ti- Fe^{3+} -Al, O-OH) isomorphism, the common presence of minute inclusions of different minerals, the appearance of radiogenic elements formed by the radioactive decay of uranium and thorium (Pb). We must also take into account the fact that the variable composition of the minerals depends significantly on the alteration processes of different kinds which take their course after the formation of the minerals, generally in hydrothermal, but also, more rarely in supergene environments.

3. Titanium-tantalum niobates are characterized, as a group, by a variety of multiform mineral species whose number exceeds 100. The main diagnostic physical features of these minerals are nearly the same, in many instances, making their diagnostic identifications difficult accordingly. Detailed studies of a series of niobates, in recent years, showed that some of these minerals, although homogeneous externally, are, in reality, mechanical mixtures [6]. Analyses of mechanical mixtures of minerals had led, in many cases, to creation of new mineral species, if composition failed to harmonize with simple stoichiometric proportions.

4. According to modern crystallochemical considerations, titanium-tantalum niobates belong to the group of complex oxides whose composition is expressed conventionally as $\text{A}_n\text{B}_p\text{X}_q$, after F. Machatschki [16], where "A" stands for cations with large ionic radii, 0.9 to 1.1 Å and larger, such as Ca, Na, U, Th, the rare earths, and, to a lesser degree, Ba, Sr, Pb, K.

The "B" category embraces, as a rule, cations with relatively small ionic radii, not over 0.7 Å, i.e. Ti, Nb, Ta, as well as Al, P, Si, and the category "X"—anions like O, OH, and F. Classification of cations like Mg^{2+} , Fe^{2+} , Fe^{3+} , Zn^{2+} , Mn^{2+} is controversial, since the size of their ionic radii is intermediate between the categories "A" and "B". It is well known that Fe^{3+} (0.67 Å) is nearer to Ti (0.64 Å) in the size of its ionic radius, while there is no question as to the Ti- Fe^{3+} isomorphism; for these reasons, Fe^{3+} belongs undoubtedly to the "B" category. As to Fe^{2+} and Mn, as well as Zn and Mg, with the example of the AB_2X_6 type of tantalite-columbite minerals, $(\text{Fe}, \text{Mn})^{2+}(\text{Nb}, \text{Ta})_2\text{O}_6$, it is evident that the divalent cations, Fe^{2+} , Mg, Mn, must be regarded as belonging to category "A". Thus iron may be either in the "A" or in the "B", depending on the degree of its oxidation. Since the coordination number of Fe^{2+} in such compounds is different from the coordination number of Ca,

Na, U, Th, it becomes desirable to divide the "A" category into two groups, "A¹" and "A²". Under such conditions, the "A¹" must include Ca, Na, U, Th, and the rare earths and the "A²"—Fe²⁺, Mn, and Mg. If so, the general formula for all titanium-tantalum niobates may be given as (A¹A²)_nB_pX_q, with the ranges of variation of n, p, and q, the atomic quantities of the categories "A", "B", and "X": n from 0.5 to 2; p from 1 to 2; q from 3 to 7.

5. There exists a close relationship between the composition and the structure of the minerals here discussed. For example, syngony of the minerals is subject to changes, depending on changes in the ratios of the atomic quantities of the "A" and "X" categories (i.e. depending on n:q), as is shown in Table 1.

Table 1. Relationship between Syngony and Composition of Tantalo-Niobates

Formula type	Examples of mineral groups	n:q	Syngony	Parameters of unit cell, Å
1. ABX ₃ or A ₂ B ₂ X ₆	Perovskite	1:3	Isometric	a ₀ = 3.8 - 3.9
2. A ₂ B ₂ X ₇	Pyrochlore-microlite	1:3.5	Isometric	a ₀ = 10.20 - 10.42
3. ABX ₄ or A ₂ B ₂ X ₈	Fergusonite	1:4	Tetragonal	a ₀ = 5.15 c ₀ = 10.89
4. AB ₂ X ₆	Euxenite, columbite, etc.	1:6	Orthorhombic	euxenite a ₀ = 5.520 b ₀ = 14.57 c ₀ = 5.166 columbite a ₀ = 5.082 b ₀ = 14.238 c ₀ = 5.730

As the ratio of atomic quantities of "A" and "X" categories increases, the syngony of the minerals becomes lower and the unit cell size becomes larger, as is evident in Table 1.

6. Differentiation of individual mineral species among minerals belonging to the same structural type must be done rationally on the basis of the principal elements of the "B" category, that is, by the proportions of Ti, Nb, and Ta. Thus niobium, tantalum, and titanium varieties may be differentiated accordingly within the range of composition of every one of the categories. The atomic quantities of Ti, Nb, Ta for every one of the known titanium-tantalum niobates are plotted on the diagram (Fig. 1). This diagram shows that most titanates contain certain quantities of niobium, even as all niobates contain certain quantities of Ti and Ta, as a rule. These relationships

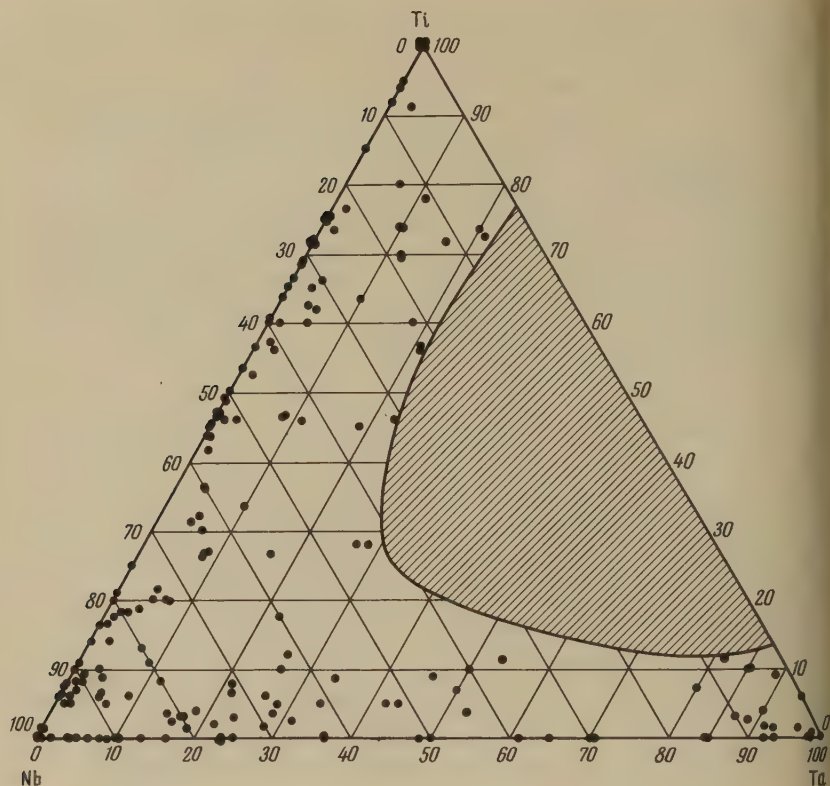


Fig. 1. Diagrammatic representation of ratios of atomic quantities of principal cations of the (Nb-Ti-Ta) group in titanium-tantalum niobates.

are expressions of a major aspect of geochemistry of niobium and tantalum: titanium has a greater affinity for niobium than for tantalum [A. I. Ginzburg, 5; E. B. Znamenskii et al., 9]. Although we find in nature practically all of the members of the continuous series, from pure niobium species to pure titanium species, as well as pure niobium to pure tantalum species, there is no such continuous grading of titanium minerals into tantalum minerals. It is not easy to say at this time whether this difference is due to a general absence of a complete isomorphous miscibility of titanium and tantalum compounds or to some differences in the geologic environments in which such compounds occur.

7. Conversions of the chemical analyses of titanium-tantalum niobates to the structural basis (on the assumption the atomic quantities of cations in the "B" category remain constant) show serious discrepancies between the empirical formulas of the minerals and their ideal and generally accepted formulas. The difference in question

is primarily of the fact that atomic quantities, n , of cations in "A" category is significantly lower than is required by the formulae ABX_3 , $A_2B_2X_7$, ABX_4 , AB_2X_6 of many minerals. On account of deficiencies in the "A" category, it should be reasonable to give the following expression to the formulas of titanium-tantalum niobates:



"x" is the deficit of the atomic quantities in the "A" category. For purposes of our inquiry into the compositional characteristics of titanium-tantalum niobates, we assembled nearly all of the published chemical analyses of these minerals and converted them to the atomic-basis. Naturally, a number of chemical analyses had to be rejected, in this connection, inasmuch as their reliability had to be questioned for many reasons. It should be pointed out that a complete chemical analysis of minerals involves great difficulties even recently:

There are no reliable methods for tantalum and niobium in the presence of large quantities of titanium.

Until recent years, there was no method for iron in different states of oxidation in the presence of uranium.

Separate determinations of elements within the rare-earths group are extremely complicated.

Errors in determinations of fluorine and of high-temperature measurements are common.

The difficulties here listed have a substantial effect on the conversion of chemical analyses into crystallochemical formulas and complicate their interpretations to a very high degree.

The isometric titanium-tantalum niobates include minerals of two different structural types which are different also in their composition: perovskite and the pyrochlore types.

Perovskite Type, ABX_3 . Perovskite structures are shown by compounds whose composition pattern is expressed by the formula ABO_3 , where "A" is Ca, Na, K, rare earths, Th, Sr, Ba, Pb, Fe^{2+} and "B" is Zr, Nb, and, more rarely, Sn, Fe^{3+} , Al. It is generally believed that compounds with perovskite structures crystallize with triclinic syngony. Studies in recent years have shown, however, that the unit cell is deformed in many compounds of this type with accompanying degradation of their symmetry.

The following minerals have perovskite structures: perovskite, zirconolite, dysanalite, loparite, irinite, nioboloparite. Ca replaces Ce, Zr, and Th isomorphously in these minerals with an accompanying replacement of Ti-Nb by Zr and Ta, but to a lesser degree. Crystals of these minerals reflect the isometric syngony, although many of them are anisotropic optically. Barth [14] determined the size of the unit cell of perovskite (3.795 Å) and of dysanalite (3.826 Å) and called these minerals pseudo-cubic. Murdoch [18] found that the unit cell of perovskite increases in size from 15.25 to 15.41 Å with increasing

quantities of niobium in the mineral, and suggested that the cubic perovskite becomes pseudo-cubic at lower temperatures. Naray-Szabo [19] showed that monocrystals of perovskite are monoclinic. The recent studies by Kay and Bailey [15] proved that the unit cell of perovskite is orthorhombic, with $a_0 = 5.37 \text{ \AA}$, $b_0 = 7.64 \text{ \AA}$, $c_0 = 5.44 \text{ \AA}$. Using BaTiO_3 crystals as the example, Megaw [17] proved that this substance is tetragonal at ordinary conditions, but becomes isometric at 200°C , confirming thereby Murdoch's supposition regarding the degradation of the symmetry of perovskite at lower temperatures. From this point of view, the changes of symmetry in perovskite are secondary phenomena. Our own studies led to the following conclusions:

1. Two subgroups of minerals need be distinguished in the perovskite group: (a) pseudo-isometric, with $a_0 = 7.64$ to 7.68 \AA (3.82 to 3.84 \AA) (perovskite, knopite, dysanalite); (b) genuinely isometric, with $a_0 = 3.84$ to 3.88 \AA (loparite, irinite).

2. Symmetry of the mineral increases with increasing quantities of niobium: the unit cell of loparite may be taken as half the unit cell of perovskite and irinite may be taken to be isometric, with $a_0 = 3.84 \text{ \AA}$. One may suppose further that presence of an isomorphous admixture of niobium in perovskite may function as a brake on the distortion of the isometric unit-cell in perovskite minerals that normally sets-in at falling temperatures.

3. Size of the unit-cell in perovskite minerals increases regularly with increasing quantities of niobium in their crystal structures. I. P. Tikhonenkov also came to the same conclusion in his recent studies of nioboloparite [12].

Pyrochlore Type $A_2B_2X_7$ This group differs from the preceding one by the presence of pentavalent niobium and tantalum ions, in place of tetravalent titanium, and by the corresponding appearance of supplementary anions, such as hydroxide and, occasionally, fluoride in the crystal structures.

The formula of minerals of this structural type is generally given as $A_2B_2O_7$. The following titanium-tantalum niobate minerals have the pyrochlore structures: pyrochlore, koppite, chalcolamprite, hatchettolite, ellsworthite, obruchevite, priazovite, blomstrandite, betafite, microlite, neotantalite, djalmaite, bismutomicrolite [N. E. Zalashkova 7], and schetelegite.

As shown by the x-ray analysis of the structures, the pyrochlore structures are found also in certain varieties of wiikite (yellow and brown), as well as in certain minerals previously classified as am-pangabeites. In addition to these minerals, there is a whole series of names occurring in the literature which are either synonyms of some others (tantalyrochlore, metasimpsonite, or pyrrhite for microlite; uranpyrochlore for hatchettolite, etc.) or else appellations of some alteration products of pyrochlore (marignacite, endeolite, hydropyrochlore, etc.).

It was demonstrated in our studies that:

a) Minerals of the pyrochlore group are found both in the definitely crystalline state and in the metamict state.

b) Varieties of the pyrochlore crystal structures do not change the size of their unit-cell after ignition. The observed differences are within the limits of error of the measurements (0.005 \AA).

c) In accordance with the principle of extinction of images, we deduced the spatial group O_h^5 -Fm $3m$, or F43 or F43m, but not the conventional Fd $3m$.

d) The structures are more perfect and the reflections are more abundant in microlites than in other minerals of the pyrochlore group. Our x-ray analyses of isometric titanium-tantalum niobates made it possible for us to ascertain that the more titanium is present in the mineral, the smaller is the size of the unit-cell. This relationship is illustrated best by the perovskite group of minerals whose unit-cell changes in direct proportion to their titanium content (Fig. 2). The same relationship is manifested clearly, on the whole, also in the pyrochlore structures (Fig. 3).

A large size unit-cell is characteristic of microlites and pyrochlores, i.e. for minerals with low titanium content. The unit-cell size of the tantalum and niobium pyrochlores varies of a more or less constant composition ($a_0 = 10.35$ to 10.42 \AA).

In the instance of minerals with a variable composition and containing titanium, uranium, and the rare earths, the unit-cell size decreases as the titanium content increases (e.g. in the case of zirconium and hafnium). The unit-cell size of the perovskite group of minerals decreases as the titanium content increases (e.g. in the case of zirconium and hafnium). The unit-cell size of the perovskite group of minerals decreases as the titanium content increases (e.g. in the case of zirconium and hafnium).

The data here cited indicate that the size of the unit-cell of isometric titanium-tantalum niobates is affected, first of all, by the size of cations in the "B" group. The more Nb and Ta is present in the minerals (ionic radii 0.69 \AA), the larger is their unit-cell size. The more Ti is present (ionic radius 0.64 \AA), the smaller is their a_0 . It becomes possible, therefore, tentatively to surmise that the titanium content of isometric titanium-tantalum niobates from the perovskite group depends on the size of the unit-cell.

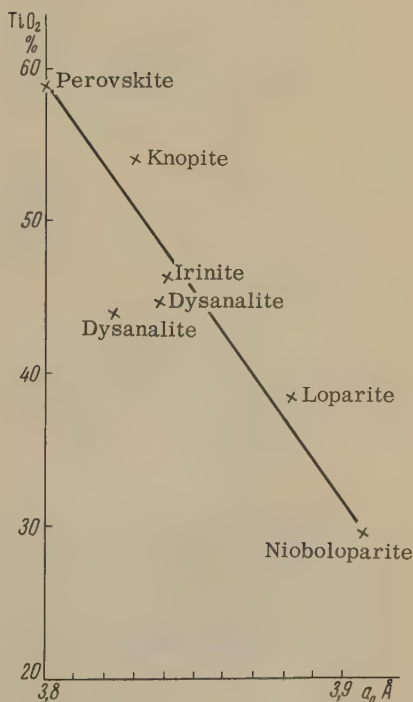


Fig. 2. Dependence of unit-cell size (a_0) on TiO_2 content in minerals of perovskite structural type.

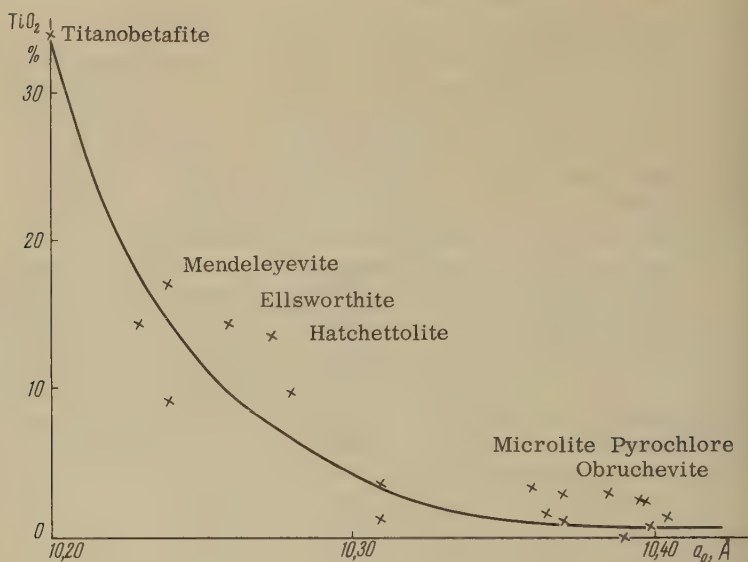


Fig. 3. Dependence of unit-cell size (a_0) on TiO_2 content in minerals of pyrochlore structural type.

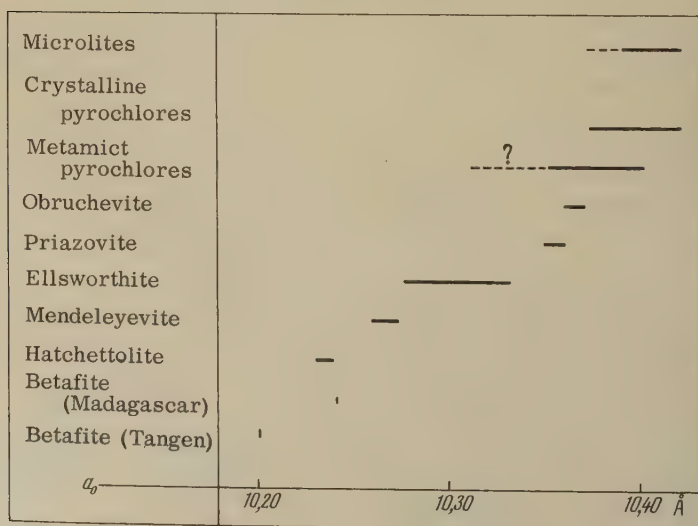


Fig. 4. Unit-cell size of minerals of pyrochlore structural type.

Considerations of the chemical composition of isometric titanium-tantalum-niobates are now made easier by the studies of L. S. Borodin and N. I. Nazarenko [2, 3, 4], who demonstrated the existence of defect structures in these minerals. Insofar as the composition of any member of the pyrochlore or the perovskite group could be represented by the general formula $A_{n-x}B_pX_q$, we were able to recalculate all of the more reliable chemical analyses of minerals in these two groups* on

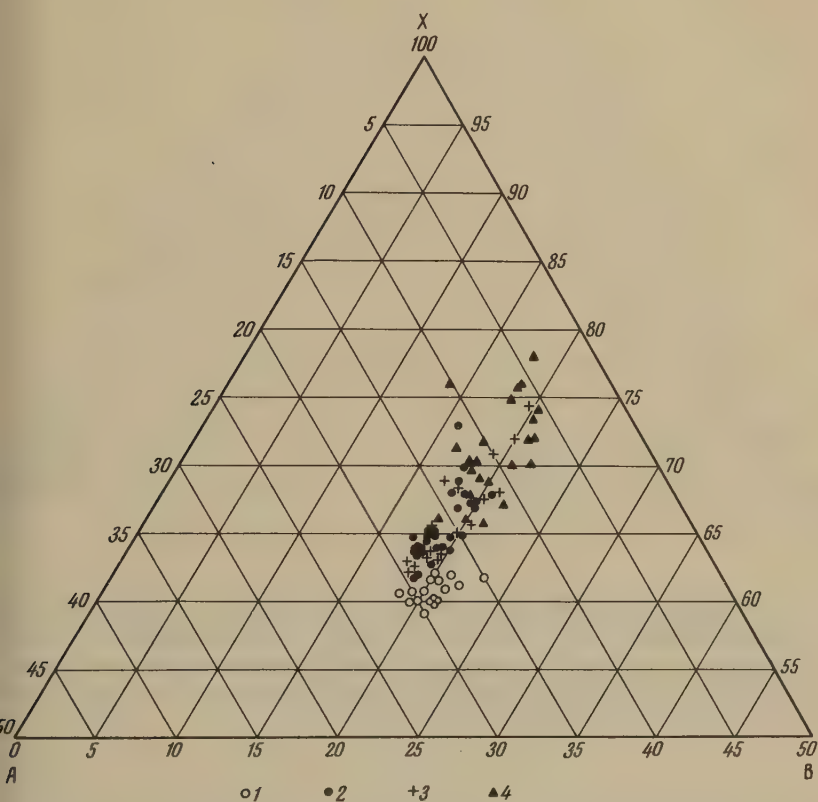


Fig. 5. Diagram showing relationships between atomic quantities in groups "A", "B", and "X" of isometric titanium-tantalum niobates. 1—perovskite, knopite, loparite, nioboloparite, irinite; 2—pyrochlore, chalcolamprite; 3—microlite, neotantalite, djalmaitite; 4—betafite, titanobetafite, hatchettolite, ellsworthite, blomstrandite, mendeleyevite, obrucheveite, priazovite, samiresite.

More than 100 analyses published in different papers were utilized in the present article. The Table shows only those for which the x-ray data were available and the size of the unit-cell was determined (see Table 3 at the end of the article).

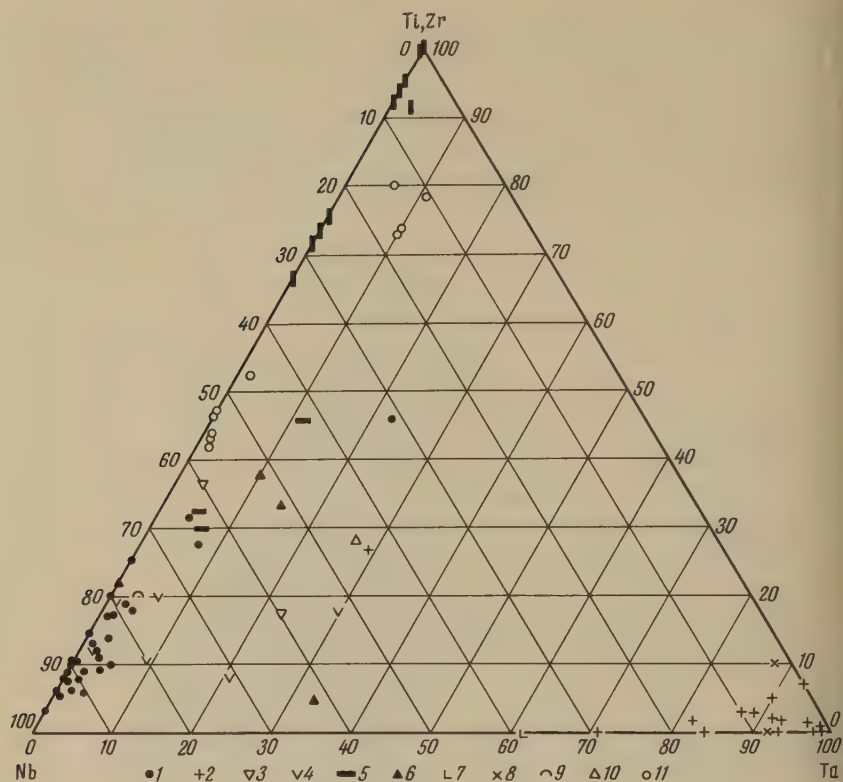


Fig. 6. Diagram showing relationships between atomic quantities of leading cations in group B (Nb-Ti, Zr-Ta) of isometric titanium-tantalum niobates. 1—pyrochlore; 2—microlite; 3—mendeleyevite; 4—obruchevite, priazovite; 5—ellsworthite; 6—hatchettolite; 7—neotantalite; 8—djalmaita; 9—samiresite; 10—blomstrandite; 11—betafite, titanobetafite.

the atomic quantity basis and to plot our results on diagrams expressing the interdependence of the leading elements in the A (Ca-rare earths—U+Th) and the B (Ti-Nb-Ta) groups, as well as the atomic quantity ratios in groups "A", "B", and "X". A study of these diagrams (Figs. 5, 6, 7) enables us to draw several important conclusions.

Diagram A-B-X (Fig. 5). Figure 5, showing the atomic ratios of ions in groups A-B-X (n:p:q), makes it evident that there are striking differences between the ratios in groups "A" and "X", but only insignificant variations in the ratios in group "B".

All of the isometric titanium-tantalum niobates may be arranged in the following series, on the basis of the n:q in the formula $A_n B_p X_q$:

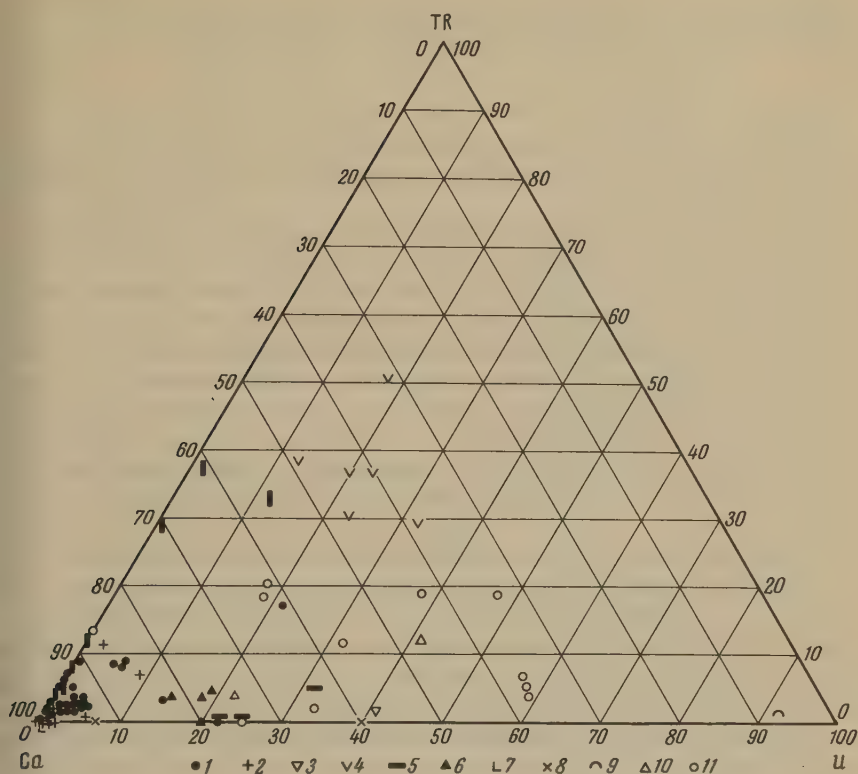


Fig. 7. Diagram showing relationships between atomic quantities of leading cations in group A (Ca-rare earths-U+Th) of isometric titanium-tantalum niobates. 1—pyrochlore; 2—microlite; 3—mendeleyevite; 4—obruchevite, priazovite; 5—ellsworthite; 6—hatchettolite; 7—neotantalite; 8—djalmaita; 9—samiresite; 10—blomstrandite; 11—betafite, titanobetafite.

Type of structure	Minerals	n:q
perovskite	1. Perovskite, dysanalite, knopite	0.25 to 0.39
perovskite	2. Loparite, nioboloparite, irinite	0.17 to 0.26
pyrochlore	3. Pyrochlore, microlite, mendeleyevite	0.21 to 0.30
pyrochlore	4. Hatchettolite, obruchevite, ellsworthite	0.14 to 0.21
pyrochlore	5. {Betafite, samiresite, blomstrandite, djalmaita, neotantalite, priazovite}	0.07 to 0.14

With the transition from perovskite to loparite and from pyrochlore to betafite, the atomic quantity of the group "A" cations grows definitely smaller, with the correspondingly decreasing n:q ratio, while the atomic quantity of the group "B" cations (p) remains more or less the same. Composition of the minerals in question cannot be expressed

therefore by the single ABX_3 or $A_2B_2X_7$ formulas; their composition is far more complex and needs be represented as follows:



Diagram Ti-Nb-Ta (Fig. 6). Examination of the ratios of atomic quantities of the group B cations (titanium-niobium-tantalum) leads to the following conclusions:

1. The microlite group is emphatically segregated in the diagram and represents an almost pure tantalum member of the series of isometric minerals here discussed. Analyses of djalmaite and neotantalite place these minerals in the microlite field. It is evident from the diagram that neotantalite is a microlite relatively high in niobium. Titanium-enriched microlites have not been found in nature.

2. Judging by the diagram, there are no uninterrupted transitions from microlite to pyrochlore in nature. This had been pointed out also by L. S. Borodin [3], in his correct explanation, namely, that pyrochlore and microlite are found in deposits of entirely different genetic types.

3. Composition of the pyrochlore-type minerals varies within a much wider range than the composition of microlites. The points representing composition of pyrochlore-type minerals in the Ti-Nb-Ta diagram are all outside the field representing the maximum of niobium. However, there is an almost continuous run of the points from the periphery of this field to the mineral varieties that are more rich in titanium and, in many cases, also in tantalum. Thus it is as if there were a continuous series from the niobium pyrochlore-proper to its titanium-enriched varieties.

4. Three groups of minerals differing in their composition may be distinguished among the isometric titanium niobates forming a solid field in the Ti-Nb-Ta diagram:

a) Varieties that are markedly enriched with niobium, are low in tantalum, and contain up to 25% of the atomic quantities as Ti. This group consists of pyrochlores, chalcolamprite, koppite, obruchevite, and samiresite. Moreover, the pyrochlores (including koppite and chalcolamprite) are characterized by the invariable presence of small amounts of zirconium.

b) Titanium-niobium varieties. This group is distinguished by its variable composition. Depending on the amounts of tantalum, the minerals may be classified as tantalum-poor (ellsworthite, betafite), minerals with appreciable tantalum (hatchettolite, blomstrandite, mendeleyevite), and tantalum-rich; the betafite from Tangen, Norway, belongs to the latter category.

5. It should be pointed out that the analyses of betafite fall within two distinctive fields in the diagram: the betafites from Madagascar are found in the same field with ellsworthites; on the other hand, the betafites from Tangen are entirely different from the Madagascar betafites in their composition. They are the titanium-richest varieties

of minerals with pyrochlore structures and it should be more fitting to call them titanobetafites. Thus apparently several minerals of a somewhat different composition were described in the literature under one name, as "betafite".

6. Minerals with perovskite structures are invariably enriched with titanium to a high degree, and they form an isolated field of their own in the Ti-Nb-Ta diagram. There are no transitions from nioboloparite to titanobetafite.

Diagram (Ca + Na)-Rare Earths-(U + Th) (Fig. 7). This diagram shows the ratios between atomic quantities of the principal cations in the "A" group in which calcium is combined with sodium and uranium with thorium. This diagram permits a differentiation of the calcium-sodium, the rare earths, and the uranium-thorium varieties of the isometric titanium-tantalum niobates. Its examination leads to the following conclusions:

1. Minerals of the microlite group are characterized by the most stable composition and by the least content of the rare earths and of uranium. There is no substantial difference between microlites and teontantalite, either in their "A" or their "B" compositions, and this latter mineral should be considered therefore to be a variety of microlite. Djalmaite, in contrast with microlite, is enriched with uranium but contains no sodium.

2. Pyrochlores consist substantially of calcium-sodium varieties, but invariably with some rare earths whose atomic quantities may be as high as 20% of the total cations in the "A" group. All pyrochlores characteristically contain rare earths of the cerium group (specifically, cerium and lanthanum) and also thorium. Koppite and chalcomprite do not differ from pyrochlores in their "A" group composition, and should be regarded therefore as varieties of pyrochlore.

3. Hatchettolite, ellsworthite, blomstrandite, mendeleyevite, and betafite are characterized by the most highly variable composition and contain appreciable quantities of rare earths and uranium together with calcium; they contain very little or no sodium. In contrast with the pyrochlores-proper, these minerals carry also yttrium and the yttrium rare earths, together with the rare earths of the cerium group. Obruchevite [A. P. Kalita, 10] and priazovite [Yu. Yu. Yurk, 13], distinguished by their high sodium and rare earths, chiefly of the yttrium group, also fall within the foregoing category. Priazovite should be regarded as a defect variety of obruchevite.

4. Samiresite stands apart from the rest of the isometric titanium-tantalum niobates, on account of its high uranium, in the "A" group, in which uranium is markedly preponderant over all of the other cations.

RECALCULATION OF CHEMICAL ANALYSES

Since the quantities of cations in the "B" group vary only within a very narrow range, as indicated in the A-B-X diagram (Fig. 5), it is justifiable to take their total quantity (p) as constant and equal 2, in the "B" group, in accordance with the structural formula $A_{2-x}B_2X_7$.

Recalculations of the more reliable chemical analyses, on the crystal-chemical basis, on the assumption of $p = 2$, show that atomic quantities of cations in the "A" group (n) are subject to variations within a wide range, from 0.5 to 2, but are generally smaller than 2, on account of the cationic deficits in the "A" group, in the majority of the minerals in question.

In respect to these deficits in the "A" group, all minerals with pyrochlore structures may be arranged as the following series:

Mineral	Atomic quant. of cations in "A" group(n)	Mineral	Atomic quant. of cations in "A" group(n)
Pyrochlore	2.00 - 1.14	Betafite	} 0.84 - 0.65
Microlite	2.00 - 1.02	(Madagascar)	
Mendeleevite	1.82	Betafite	} 0.70 - 0.58
Ellsworthite	1.40 - 1.17	(Norway)	
Hatchettolite	1.30 - 0.90	Djalmaite	0.64
Obruchevite	1.16 - 1.12	Samiresite	0.58
Priazovite	0.96 - 0.78	Neotantalite	
Blomstrandite	0.86 - 0.77		

It is easy to divide these results for the "n" into three categories, with the atomic quantities of the "A" group cations ranging from 2.0 to 1.5, from 1.5 to 1.0, and from 1.0 to 0.5. Certain varieties of pyrochlore and microlite whose composition is close to the ideal one ($A = 1.50$ to 2.00), as well as some other varieties with a conspicuous deficit of the cations, attract our attention at once.

As illustrated by the diagrams (Figs. 8 and 9), there is a definite relationship between magnitudes of the cation deficit, in the "A" group, and the content of Ti, Zr, U, and Th of the mineral. Minerals high in titanium and uranium show invariably a high deficit of the group "A" cations. L. S. Borodin explains these deficits as being due to the following two circumstances:

a) A compensation of valencies in the "A" group accompanying the replacement of pentavalent niobium by tetravalent titanium by the means of a withdrawal of the corresponding quantity of the group "A" cations.

b) A leaching-out of sodium and calcium during the subsequent mineral-alteration processes.

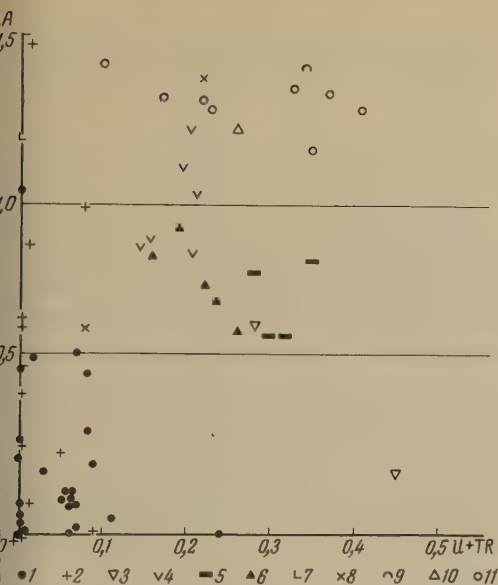


Fig. 8. Dependence of the deficit of the group "A" atomic quantities on uranium and thorium content of the mineral. 1—pyrochlore; 2—microcline; 3—mendeleyevite; 4—obruchevite, triazovite; 5—ellsworthite; 6—hatchettolite; 7—neotantalite; 8—djalmaitite; 9—samiresite; 10—blomstrandite; 11—betafite, titanobetate.

It is essential here to point out that all minerals with a high deficit of the group "A" cations are characterized by a high content of water which is parted from them at 150 to 250 C. The entry of water into such minerals is related apparently to the leaching-out of some of the group "A" cations.

Also, we must point out that the minerals showing high deficits of the cations are found invariably in the metamict state, while minerals without deficits in the group "A" cations (microclites and many of the pyrochlores) are crystalline, as a rule. A problem presents itself accordingly: is there not a relationship between

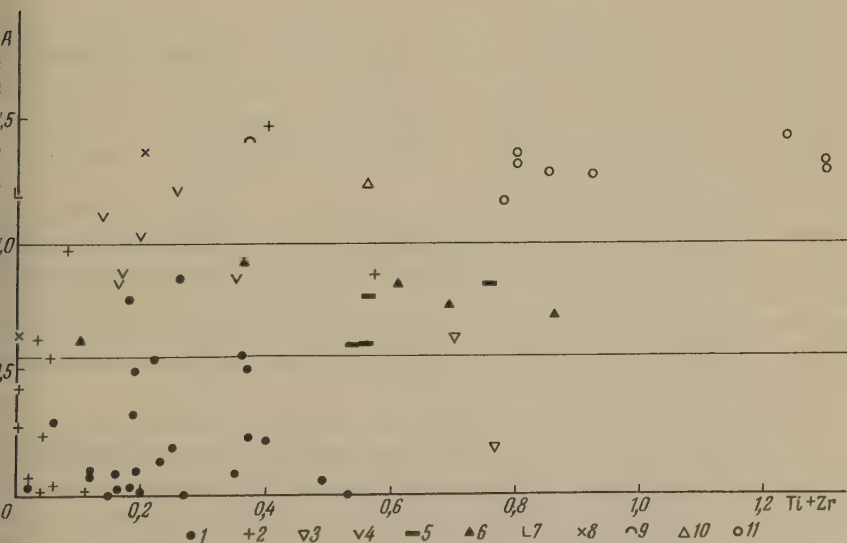


Fig. 9. Dependence of the deficit of the group "A" atomic quantities on titanium and zirconium content of the mineral. Key: Same as in Figure 8.

these two phenomena? Is there not a possibility that the metamictic degradation of titanium-tantalum niobates is facilitated by such defects in their structures?

CLASSIFICATION OF ISOMETRIC TITANIUM-TANTALUM NIOBATES

A reasonable classification of isometric titanium-tantalum niobates may be proposed here, on the basis of the proved relationships between their composition and structures. This classification differs somewhat from the existing one [J. D. Dana et al., 8], and it is developed rationally on the following premises:

1. *Structural Type of Mineral.* All isometric titanium-tantalum niobates are divided into two distinctive structural types, as we had shown: The perovskite, $A_{2-x}B_2X_6$, and the pyrochlore, $A_{2-x}B_2X_7$.

2. *Cation Ratios in the "B" Group.* Depending on the preponderant cation, the following mineral series may be distinguished, for example within the pyrochlore structural type:

- a) The tantalum microlite series: $A_{2-x}Ta_2X_7$;
- b) The niobium series, with small quantities of titanium (the pyrochlore group): $A_{2-x}Nb_2X_7$;
- c) The titanium-niobium series (the hatchettolite group): $A_{2-x}(Nb, Ti)_2X_7$;
- d) The titanium series (the titanium-betafite group): $A_{2-x}(Ti, Nb)_2X_7$.

Every one of the foregoing series is characterized by a certain definite size of its unit-cell, the a_0 .

The perovskite structural type may be likewise differentiated into the following series: (a) the niobium-tantalum (the loparite group): $A_{1-x}(Ti, Nb)O_3$; (b) the titanium (the perovskite group): $ATiO_3$. Such differentiation is in harmony also with the symmetry of these mineral series since the niobium-tantalum series are isometric and the titanium series are pseudo-isometric.

3. *Cation Ratios in the "A" Group.* There are wide fluctuations on occasions, in the composition of minerals within the series. For this reason, a more detailed classification of mineral species within the series needs be based on the cations preponderant in the "A" group of the constituents; that is, we should recognize the sodium-calcium, the uranium-calcium, and the rare earths-uranium-calcium members of the series.

4. *Deficits in the "A" Groups.* Insofar as there is an appreciable variation in the composition of even one and the same mineral species in regard to the group "A" cations, on account of the leaching-out of the cations and on account of certain other processes, we are faced with the necessity of the recognition of varieties of the minerals within one and the same species. This is facilitated by the conversion of the chemical analyses to the crystal-chemical basis, as formulas, where

Table 2. Isometric Titanium-Tantalum Niobates

Structural type		A. Pyrochlore, $A_2X_6B_2X_7$						B. Perovskite, $A_2XB_2X_6$	
Mineral series	1. Tantalum	II. Niobium		III. Titanium-Niobium		IV. Titanium		Niobium-Titanium	Titanium
	B - Ta	B - Nb(Ti)		B - Nb, Ti		B - Ti(Nb)		B - Ti, Nb	B - Ti(Nb)
	Microcline	Pyrochlore		Hatchettolite		Titanobetafite		Loparite (isometric)	Perovskite (pseudo-isometric)
	Microcline	Pyrochlore		Hatchettolite		Titanobetafite		Loparite	Perovskite
Varieties of minerals	A = 2.0 - 1.5	A. Ca, Na, CeRE, Th		A. Ca, Na, U, YRE, RE		A. Ca, U, YRE		A. Ca, RE, CeRE	A. Ca, RE, CeRE
	A = 1.5 - 1.0	Pyrochlore		Obrucheveite		Mendeleyevite		Loparite, nioboloparite	Perovskite, knopite, dysanallite
	A = 1.0 - 0.5	Pyrochlore Chalcoprite		Obrucheveite		Ellsworthite hatchettolite		Irrite	
Size of unit - cell		Djalmaite		Priazovite		Blomstrandite, betafite			
		$a_0 = 10.42 - 10.37 \text{ \AA}$		$a_0 = 10.42 - 10.35 \text{ \AA}$		$a_0 = 10.32 - 10.23 \text{ \AA}$		$a_0 = 3.88 - 3.84 \text{ \AA}$	$a_0 = 3.84 - 3.82 \text{ \AA}$

Note: Nectantalite, djalmite, samiresite were identified previously, each on the basis of only one chemical analysis [J. Dana et al., 8], their existence is in doubt.

Translator's Note: "RE" means "rare earths";

YRE - "rare earths of the yttrium group";

CeRE - "rare earths of the cerium group".

Table 3. Chemical Analyses of Minerals of Pyrochlore Structural Type

Mineral	Microlite							Pyrochlore			Kopple
Source	Vir- ginia	Nor- way	China	Brazil	Toisk- hem	Donker- hoek	Nor- way	USSR	Kola	Ural	Kaise- stuhl
X-ray	Arnott	Bjør- lykke	Sidor- enko	Kerr, Holmes	Shaub	Reun- ing	Bjør- lykke	Sidor- enko	Sidor- enko	Sidor- enko	Bræn- den- berge
Analysis	$a_0 =$ 10.42Å	$a_0 =$ 10.41Å	$a_0 =$ 10.40Å	$a_0 =$ 10.40Å	$a_0 =$ 10.39Å	$a_0 =$ 10.37Å	$a_0 =$ 10.36Å	$a_0 =$ 10.40Å	$a_0 =$ 10.39Å	$a_0 =$ 10.37Å	$a_0 =$ 10.37Å
	1	2	3	4	5	6	7	8	9	10	11
Na ₂ O	2.86	3.26	5.27	-	3.37	0.72	3.68	4.64	-	4.86	2.83
K ₂ O	0.29	0.64	0.08	-	0.41	0.21	-	0.06	-	-	1.64
CaO	11.80	10.48	8.60	15.48	15.03	6.79	13.84	12.70	13.22	18.89	15.84
MnO	-	-	0.08	-	-	0.51	-	0.017	-	trace	0.01
FeO	-	2.77	0.32	1.24	-	-	8.25	1.11	-	-	-
MgO	1.01	0.34	-	-	0.07	0.27	1.14	not deter.	0.55	-	0.21
SumY ₂ O ₃	0.23	-	0.18	-	0.35	1.07	-	1.79	2.78	1.74	-
SumCe ₂ O ₃	0.17	0.50	-	-	0.26	0.55	2.06	-	-	-	9.84
UO ₂	1.59	4.21	-	-	0.77	4.03	-	-	-	-	-
UO ₃	0.30	-	-	-	0.17	-	-	-	-	-	-
U ₂ O ₈	-	-	-	-	-	-	-	3.01	-	trace	-
SnO ₂	1.05	-	-	-	1.61	0.38	-	-	-	-	-
TiO ₂	-	-	-	-	-	0.26	-	1.89	-	-	-
SiO ₂	-	-	-	0.75	-	0.13	1.51	0.32	-	1.52	-
Fe ₂ O ₃	0.29	-	-	-	-	0.92	-	-	2.25	0.86	9.75
Al ₂ O ₃	0.13	-	0.45	0.83	-	-	-	-	-	-	-
TiO ₂	-	1.58	0.05	0.83	-	1.07	1.61	2.64	3.05	3.60	0.75
ZrO ₂	-	-	-	-	-	0.30	0.12	2.00	-	-	0.61
Nb ₂ O ₅	7.74	trace	0.08	5.45	3.56	2.65	62.77	59.63	-	62.52	56.43
Ta ₂ O ₅	68.43	73.72	79.72	74.37	74.27	72.38	-	4.38	53.28	3.20	0.15
CuO	-	-	-	-	-	0.05	-	-	-	-	-
SrO	-	-	-	-	-	0.70	-	0.84	-	0.04	-
Bi ₂ O ₃	-	-	3.25	-	-	0.42	-	-	-	-	-
PbO	-	-	-	-	-	0.36	-	0.12	0.22	-	-
BeO	0.34	-	-	-	-	-	-	-	-	-	-
P ₂ O ₅	-	-	-	-	-	-	-	0.08	-	-	-
CO ₂	-	-	-	-	-	-	-	0.40	-	-	-
BaO	-	-	-	-	-	-	-	-	-	0.21	-
F	2.85	-	2.00	1.29	-	-	-	0.25	-	4.10	1.53
H ₂ O ⁺	1.7	0.39	0.60	-	0.27	5.94	5.02	1.51	2.61	0.41	1.09
H ₂ O ⁻	-	2.33	-	-	-	-	-	0.64	-	-	-
n.n.n.	-	-	-	-	-	-	-	2.20	-	-	-
Sum	100.25	100.22	100.70	100.24	100.14	99.71	100.00	100.227	-	101.95	100.81
Sp. Gr.	5.656	5.82- 5.93	6.426	-	6.41- 6.42	5.06	-	-	4.13	4.29	-
Citation	Dana et al.	Shub- nikova	Zalash- kova	Pough	Dana et al.	Dana et al.	Dana et al.	Pozhar- itskaya	Sobo- leva	Bonsh- tedt- Kuplet- skaya	Dana et al.

upon, by the group "A" atomic quantities, it becomes possible to differentiate between the saturated, the weakly defective, and the strongly defective varieties ($A = 1.5$ to 2.0 , 1.0 to 1.5 , and 0.5 to 1.0 respectively).

The proposed classification of isometric titanium-tantalum niobate is presented in Table 2.

Table 3 (Continued)

Mineral	Obruchevite			Priazovite	Betalite		Hatchettolite			Ellsworthite	Mendeleyevite
Source	Kola	Kola	Ukraine	Ukraine	Madagascar	Tangen	Hybla	Kola	China	Hybla	Baikal
	Sidor-enko	Sidor-enko	Sidor-enko	Sidor-enko	Bar-sanov	Björlykke	Bar-sanov	Sidor-enko	Sidor-enko	Björlykke	Sidor-enko
x-ray analysis	$a_0 = 10.37\text{\AA}$	$a_0 = 10.36\text{\AA}$	$a_0 = 10.36-10.35\text{\AA}$	$a_0 = 10.36\text{\AA}$	$a_0 = 10.28\text{\AA}$	$a_0 = 10.20^*(10.29)\text{\AA}$	$a_0 = 10.29\text{\AA}$	$a_0 = 10.24\text{\AA}$	$a_0 = 10.23\text{\AA}$	$a_0 = 10.28\text{\AA}$	$a_0 = 10.26\text{\AA}$
	12	13	14	15	16	17	18	19	20	21	22
Ti_2O_3	2.43	0.18	-	-	-	-	-	-	1.44	-	-
TiO_2	0.31	0.02	-	-	-	-	-	-	0.60	-	1.70
Nb_2O_5	2.82	4.92	4.67	3.21	3.45	6.62	13.62	5.56	6.31	11.73	13.41
Ta_2O_5	0.35	0.21	0.09	1.00	-	-	0.43	-	0.31	0.43	-
FeO	-	-	-	0.20	-	-	-	-	-	-	1.12
Fe_2O_3	0.26	0.14	0.79	1.15	0.40	-	0.20	-	0.18	-	0.26
MnY_2O_3	11.34	13.42	7.16	4.78	0.90	3.90	0.62	1.15	5.90	0.21	0.95
MnCe_2O_3	0.66	1.97	0.75	0.10	0.60	2.06	0.50	-	0.00	-	25.85
O_2	-	5.14	-	trace	-	-	5.72	5.39	1.28	18.50	-
O_3	9.72	4.83	11.70	13.93	26.60	9.64	5.08	16.00	15.13	-	-
O_6	-	-	-	-	-	-	-	-	-	0.10	-
O_2	-	0.75	-	-	0.30	-	1.46	-	-	-	-
O_2	0.26	4.69	0.60	0.82	1.30	0.12	0.42	0.98	0.25	2.54	1.50
O_2	3.78	1.99	3.13	2.36	-	0.42	1.56	2.69	3.55	4.10	-
Fe_2O_3	4.30	6.31	5.20	4.68	2.87	6.24	3.63	4.64	1.73	0.42	-
O_3	-	0.47	1.44	3.21	2.10	1.20	-	-	1.35	10.47	13.55
O_2	6.29	3.29	2.54	5.36	18.30	32.27	8.82	9.04	14.28	-	-
Fe_2O_3	-	0.13	-	-	-	-	5.90	6.32	-	-	-
O_2O_5	37.54	45.28	30.58	24.67	34.80	11.75	31.70	42.02	16.43	34.22	37.40
O_2O_5	5.47	2.07	15.02	22.98	trace	11.95	15.28	-	19.88	4.32	-
O_2	-	-	-	-	-	-	-	-	-	-	-
O_2	-	-	-	-	-	-	-	-	trace	-	-
O_3	-	-	-	-	-	-	-	-	-	-	0.64
O_2	-	-	3.32	1.53	trace	0.33	0.24	1.58	0.31	0.24	-
O_2	-	-	-	-	-	-	-	-	-	-	-
O_5	-	-	-	-	-	-	-	-	-	-	-
O_2	-	-	-	-	-	-	-	-	-	-	-
O_2	-	0.55	-	-	-	-	-	-	1.13	0.22	2.00
O_2	-	0.42	-	-	-	-	-	-	-	-	-
O^+	6.48	3.29	9.21	6.53	7.60	13.59	5.05	3.90	6.15	12.22	-
O^-	7.77	0.53	-	3.37	-	-	-	-	3.31	-	-
H_2O	-	-	-	-	-	-	-	-	-	-	-
H_2O	99.78	100.60	96.26	99.88	99.22	100.09	100.23	99.27	99.52	99.72	99.38
H_2O	3.60-3.80	4.79	-	4.66	-	-	4.417	4.82	-	3.608	4.762
Location	Kalita	Kupriyanova	Bar-sanov	Yurk	Dana et al.	Shubnikova	Soboleva	Soboleva	Ssu-yu-Dung	Soboleva	Soboleva

obtained by calculations of inter-planar distances in x-ray diffraction patterns of pure material.

It should be emphasized that the mineral groups here distinguished were found separately in deposits of different genetic types and their composition is characteristically different for that reason. Thus minerals of the microlite group are found only in pegmatites of the sodium-lithium type in which they are crystallized only during the terminal and final stages of albitization and lepidolitization when the

residual solutions are strongly enriched with tantalum and, as a rule, contain practically no titanium, uranium, and the rare earths. In many instances, microlites are crystallized after tantalites, manganotantalites, stibiotantalites, and bismutotantalites and, indeed, constitute definite replacements of these minerals [A. Ginzburg, 5]. We should point out, in this connection, that entries of appreciable quantities of Na, often with admixtures of Sb and Bi, which are not fixed by minerals of the other groups, are common and typomorphic for microlites.

Minerals of the pyrochlore group are found most commonly in syenite and nepheline-syenite pegmatites, metasomatic albitites, and carbonatites, i.e. in the post-magmatic formations related to intrusions of alkali rocks; appearance of the pyrochlore group is highly diagnostic, in connection with the albitization and the carbonatization processes.

Their composition is characterized by the high amounts of Na, the invariable presence of the rare earths of the cerium group (chiefly cerium, lanthanum, neodymium, and, to a lesser extent, praesiodymium), thorium, and zirconium. Among the carbonatites, one may find occasionally varieties with relatively high amounts of uranium and tantalum ($\text{Nb}:\text{Ta} = 10:1$). Sr and Ba are their typomorphic admixtures.

Minerals of the obruchevite and the priazovite type are found in albitized muscovite-beryl pegmatites enriched with uranium and the rare earths of the yttrium group, as is shown by their composition. In a series of cases, these minerals are developed after the earlier niobates of the columbite type whom they may replace quantitatively.

Minerals of the hatchettolite and betafite groups are found in uranium-rare earths oligoclase-microcline-biotite pegmatites enriched in rare earth silicates and in various titanium niobates of the euxenite-polycrase, fergusonite, samarskite-khlopinita, and other types. There is no direct relationship between the occurrence of these minerals and the albitization process in the pegmatites, although these minerals are formed later than many other titanium niobates and are definitely replacing them, in a large number of instances. Their uncommonly varied composition may be explained possibly by such origins. Consequently, the composition of isometric titanium-tantalum niobates is expression of the environments in which they were formed.

We may draw the following conclusions from our studies of compositions and structures of isometric titanium-tantalum niobates:

1. The minerals in question differ among themselves significantly in the atomic proportions of the groups "A" and "X" cations while they have only minor variations in the group "B" atomic quantities of their cations.

2. On the basis of the cation ratios in the "A" and the "B" groups we propose a classification of isometric titanium-tantalum niobates affording recognition of the mineral species and of their varieties.

3. We proved the relationship between the size of the unit-cell (a_0) and the composition of the minerals, chiefly their titanium content.

4. Among minerals of the pyrochlore structural type, we distinguish their varieties whose chemical composition is very close to the ideal ($A = 2.0$ to 1.5), as well as varieties showing conspicuous deficits of the group "A" cations.

Minerals with a large deficit of the group "A" cations are high in niobium, uranium, and water, and are generally found in the metamictic state.

5. With the foregoing considerations in mind, the formulas of isometric titanium-tantalum niobates may be represented rationally as follows:

(a) The pyrochlore structural type: $A_{2-x}B_2X_7$;

(b) The perovskite structural type: $A_{1-x}BX_3$ or $A_{2-x}B_2X_6$.

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THE CHEMISTRY OF AEGIRINIZATION AND NEPHELINIZATION
OF PYROXENE IN THE FORMATION OF METASOMATIC
NEPHELINE-PYROXENE ROCKS (IJOLITES)

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In petrographic literature, the problem of origin of alkalic rocks is generally reduced to enquiries into environments of formation and differentiation of alkalic magma and also to its relationship to granitic or basaltic magma. It has been shown petrographically in several instances, however, that the origin of alkalic rocks may be fundamentally different and that alkalic rocks may be formed heterogenetically, i.e., by metasomatic transformations of other rocks whose origin is unrelated to intrusion or crystallization of alkalic magma. Nephelinization plays a leading part in such transformations [4]. The author has suggested, in his recent publication [2], that leucocratic and melanocratic analogues of ijolites and ijolites themselves may be metasomatically altered, nephelinized pyroxenites, in most zoned bodies of ultrabasic alkalic rocks.

Petrographically, metasomatic transformation into a metasomatic rock of the ijolite-melteigite type amounts to an initial replacement of part of the primary pyroxene by nepheline and a "greening" of the pyroxene, because of entry of some aegirine molecules into its composition. In other words, an aegirinization process of the pyroxene (of diopside or of augite) takes place. The alteration of pyroxene consists of 1) a degradation of its crystal lattice which accompanies the dissolution of some of the mineral grains, and 2) its partial transformation as the result of the replacement of some cations by others. These latter effects are clearly evident from comparisons between the chemical composition of the fresh and the aegirized pyroxene, as well as from the morphologic characteristics resulting from aegirinization. By using the color-change of the originally colorless or brownish pyroxene (in thin sections) as an indicator of aegirinization, we may assume that a definite relationship exists between the "greening" of pyroxene and increase in alkali content, as reported by many investigators. Comparisons of chemical composition and optical properties of pyroxenes from different parts of ultramafic-alkalic bodies confirm this assumption.

Aegirinization is not definitely associated with any one of the crystallographic directions in the primary pyroxene crystals (e.g. fissure planes, etc.). The aegirized areas, consisting of variously shaped

spots and bands, are unrelated to the cleavage planes. Also aegirinization is not confined to peripheral margins as observed by the earlier investigators in their petrographic studies of ijolites-melteigites. This shows that aegirinization depends on the diffusion of different cations in the pyroxene crystal structures and on their accessions to and withdrawals from the crystal without disturbances in the crystal structures as a whole.

Nephelinization is caused by the action of endogenic alkaline solutions on pyroxene. Such solutions, enriched with sodium, aluminum, and other constituents bring about alteration of the crystal. The reaction may be stated as follows: pyroxene c + (Na) \rightarrow aegirized pyroxene + (Ca). (1)

Comparison of chemical composition of aegirine, $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ and of primary pyroxene, generally a diopside, $\text{Ca}(\text{Mg}, \text{Fe}^{2+})\text{Si}_2\text{O}_6$, indicates that replacement of calcium by sodium, in the pyroxene crystal, results in lowering the overall positive valence. So as to compensate this valence deficiency caused by the exchange of Ca^{++} for Na^+ , concurrent ionic exchanges must occur involving isomorphous replacements of low valence cations in the crystal structure by higher valence cations. Chemical analyses of pyroxene from pyroxenites of different parts of ultramafic alkalic bodies show that it contains both ferrous and ferric iron, as well as alumina. Consequently, formation of the aegirine molecule does not necessarily depend on accessions of iron from extraneous sources or on the isomorphous replacement of Fe^{3+} by Mg^{2+} . One may assume, for example, a parallel replacement of Al^{3+} by Mg, i.e., a jadeization of pyroxene.

However, there is no correlation either between Al and Fe^{3+} or between Al and Na, in published analytical data on pyroxene. As a rule, the alumina content is too low to compensate for the simultaneous entry of both alkalis and trivalent iron into pyroxene structures. Taking account of the foregoing considerations, we may suggest a different and more probable explanation of aegirinization as a reaction involving oxidation of the divalent iron by the action of sodium-bearing alkaline solutions on pyroxene.

The common oxidation-reduction potential of the reaction $\text{Fe}^{2+} = \text{Fe}^{3+} + e$ is + 0.77 V. (It is also the same for certain other oxidation-reduction reactions.) This magnitude is diminished markedly, in our case, at more alkaline pH, especially on transition from acid to neutral or to weakly alkaline media. Thus, according to B. Meson, the magnitude of E_0 of the reaction $\text{Fe}^{2+} = \text{Fe}^{3+} + e$ falls down to -0.2 V at pH 8 and to -0.3 V at pH 10, etc. [3].*

These findings enable us to presume the possibility of the oxidation of iron in pyroxene under the action of alkaline solutions. Also, the course of the reaction $\text{CaFe}^{2+}\text{Si}_2\text{O}_6 + (\text{Na}) = \text{NaFe}^{3+}\text{Si}_2\text{O}_6 + (\text{Ca})$ depends

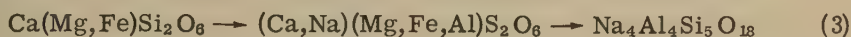
*See Fig. 21, p. 144, in Mason, B., 1952, Principles of Geochemistry, John Wiley and Sons, New York, 276 pages.

directly on the concentration of sodium in the solution. An increase in the concentration of sodium is conducive to the formation of aegirine, i.e. to the conversion of the divalent iron into trivalent iron.

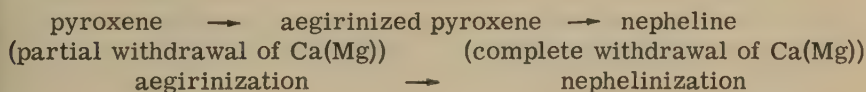
Aegirization differs fundamentally from nephelinization in which there is a complete destruction of the pyroxene crystal lattice resulting in the dissolution of pyroxene and in its replacement by nepheline:



The main result of this reaction is the entry of alumina and alkalis into silicate rock structures accompanied by a complete "displacement" of calcium, magnesium, and other cations from the original pyroxene into solution. Assuming that such displacement is gradual, at least in its early stages, one may further assume that the transition from $\text{Ca}(\text{Mg}, \text{Fe})\text{Si}_2\text{O}_6$ to $\text{Na}_4\text{Al}_4\text{Si}_5\text{O}_{18}$, * from pyroxene to nepheline, involves formation of an intermediate compound, $(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}, \text{Al})\text{Si}_2\text{O}_6$:



By comparing reactions (1) and (3), one concludes that the hypothetical "intermediate compound" may be an aegirized diopside or an aegirite. Consequently, nephelinization (3) may be expressed by the following reaction:



As a rule, pyroxenite is highly variable in its grain size. The infiltration of solutions into this rock should be highly variable accordingly. Insofar as the replacement of pyroxene by nepheline takes place only as a function of the dissolution of pyroxene, the progress of nephelinization is irregular, because only a part of the pore space of the rock is filled by the reacting solutions. The resulting nephelinization "nuclei" determine further developments of the process. These relationships may serve to explain the petrographic characteristics of ijolite-melteigites; their irregularity of quantitative mineralogical composition, the alternations of essentially nepheline and essentially pyroxene areas (even within the same small rock fragment, and the presence of relicts of aegirized pyroxenite.

At the same time, aegirization involves a much greater volume of the rock, on account of the diffusion halo of sodium in pyroxene crystal structures. In this manner, nephelinization and aegirization, the two processes of the metasomatic alteration of pyroxene, are essentially concurrent. Their end product is a rock of the ijolite type consisting of nepheline and relict aegirized pyroxene.

*The chemical formula of nepheline is given here corresponding to its structural formula, $\text{Na}_4\text{Al}_3(\text{AlSi}_5\text{O}_{18})$, as determined by N. V. Belov [1].

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DISCUSSION

The Number of Factors of State in Systems

(A reply to I. V. Alexandrov*)

There is a statement of disapproval of my formula for the number of independent parameters of a system at equilibrium, or of the "number of the factors of state" [3, 4, 5], in the article by I. V. Alexandrov [1]. Let us consider now the pertinent concepts of thermodynamics.

What are the thermodynamic factors of state? The term "parameter" means simply a variable. Some writers identify thermodynamic parameters as thermodynamic variables, such as thermodynamic magnitudes, thermodynamic properties, thermodynamic factors, etc. The thermodynamic parameters of state are the magnitudes that are descriptive of the macroscopic state of a thermodynamic system. Among the magnitudes employed in thermodynamic equations, only the magnitudes irrelevant to the state of the system at the given time but pertinent to the history of the system, such as the heat absorbed or the work performed by the system, cannot be included with the parameters of state. If the system has gone through a cyclic process and has returned to its original state, all of its parameters of state assume their initial magnitudes [2].

Parameters of state are classified as intensive (temperature, pressure, chemical potentials, concentrations of constituents, and others) and extensive, i.e. dependent on the mass (volume, entropy, masses of components or of phases, and others).

At an equilibrium state of a system, only a limited number of the parameters of state have independent magnitudes, while the rest of the parameters are functions of these independent ones. I proposed to call each independent parameter, at an equilibrium state, "the factors of the equilibrium state" of the system or, in brief, "the factors of state" or "the factors of equilibrium" [3, 4].

As we know, the Phase Rule of Gibbs, in its application, is suited only to intensive parameters of the system. On the whole, W. Gibbs attached no particular importance to extensive parameters, such as the mass of phases or of systems (the appropriate passage from Gibbs cited by I. V. Alexandrov was also cited by me [5, p. 8]). There has developed a now traditional neglect of the extensive parameters among some physical chemists, owing to the influence of Gibbs. One comes across writers who treat only intensive parameters as the parameters of state, on the principle that the equilibrium of a system is not affected by any change in its extensive parameters, such as the mass

*See Geochemistry (Geokhimiya) No. 3, 1958, p. 353.

of phases or the mass of the system [A. V. Storonkin, 7, p. 78]. Such definition of the parameters of state is out of harmony with the concept of "state" in its generally accepted sense in physics and thermodynamics. Thus the basic "function of state", in thermodynamics, is the internal energy, U , whose complete differential has the following expression:

$$dU = TdS - pdV + \mu_a dm_a + \dots + \mu_k dm_k. \quad (1)$$

It is evident from this fundamental equation of thermodynamics that the function of state, U , is a function of the extensive parameters: V , volume of the phase; S , its entropy; and m_a, \dots, m_k , the masses of the components. The internal energy of a multiphase system is the sum of internal energies of its phases, i.e. is a function of the phase mass. Inasmuch as the term "function of state" is generally accepted, in its reference to the internal energy and to other thermodynamic potentials, the arguments of these functions, both intensive and extensive, including the masses of components, phases, and systems, must be termed "the parameters of state". In a description of the state of a system in which a chemical reaction is taking place, it is the masses of the phases, in the process of formation, whose importance is cardinal and it is the masses that are the most important parameters of state of the system. We may also remark that examples of the parameters of state given by all textbooks on the principles of thermodynamics are all extensive parameters, such as volume, entropy, and masses of components.

According to I. V. Alexandrov, only intensive parameters may be considered as the factors of equilibrium, whereas extensive parameters, particularly masses of components, must not be so considered, "since masses of components do not serve to define the equilibrium in a system" [1]. And yet the term, "factors of equilibrium", is used by me as an abbreviation, devoid of felicity as it may be, in place of the term "the factors of the state of equilibrium." As to the state of equilibrium itself—it depends undoubtedly on masses of the components. Indeed, the phase state of a system varies, depending on variations of masses of the components and both temperature and pressure of a system vary, depending on variations in the masses of the components, at a given volume and a given entropy.

The principal objections of I. V. Alexandrov are due to my equation for the total number of factors of the state of equilibrium of a system, f_{in} and f_{ex} , the intensive and the extensive ones, i.e. for the maximum number of mutually independent parameters of state. Namely, for a simple system (not taking into account electric, surficial, and other forces):

$$f_{in} + f_{ex} = k + 2 \quad (2)$$

where k is the number of components of the system.

The " $k + 2$ " parameters fully define the state of the system,

provided the number of phases is $\phi \leq f_{\text{ex}}$. If $\phi > f_{\text{ex}}$ and if, consequently, $n < f_{\text{in}}$, where n is the number of degrees of freedom, we are dealing with an indefinite transitional state involving inter-related magnitudes of the intensive factors of state. Only under such transitional and indefinite conditions, in an equilibrium system, is there a possibility of reversible processes while the intensive parameters remain constant [5, p. 25 and pp. 29-30].

In the case of a single-phase (homogeneous) system, the dependance of its state on the " $k + 2$ " factors constitutes one of the fundamental principles of thermodynamics, as stated in the basic equation (1). The proof that the same number of factors of state holds also for multi-phase equilibrium systems is so simple that equation (2) looks like a tautology. Curiously, however, insofar as I know, this simple and useful relation is never found in the basic treatises on thermodynamics and had to be derived independently by myself [3, 4], in connection with the development of thermodynamic premises for the analysis of the parageneses of minerals. The novelty here consists in the fact that I was led to assign a greater importance to the extensive parameters, including the masses of phases as well as of systems, than is traditionally the case in theoretical chemical thermodynamics. It was this departure from tradition that was displeasing to I. V. Alexandrov.

Contrary to the opinion of I. V. Alexandrov, I do not try to replace the Phase Rule of Gibbs by my equation (2) (as if to produce "the Phase Rule without the phases", [1]). The Phase Rule of Gibbs and the concept of the number of degrees of freedom of the system $n = k + 2 - \phi$ are employed by me in their ordinary sense and extensively, in my papers, as foundations for the analysis of mineral parageneses. However, in applications of the Phase Rule, it is admitted that systems are not bound by any extensive factors of state. If, on the other hand, the state of a system depends on fixed values of the equilibrium factors, the Phase Rule must be used in conjunction with equation (2). For example, in the instance of closed systems, in which the masses of the " k " components are given, the number of degrees of freedom cannot exceed 2, regardless of the number of components and phases ("the GEMM Theorem"). Since " $k + 2$ " parameters—the volume, the entropy, and the masses of the " k " components—are fixed for any isolated system at equilibrium, no changes whatsoever are possible in such a system, according to equation (2), regardless of the number of components and phases. Under such conditions, the Phase Rule proves to be inadequate as a basis for considering the truly possible variations of the system, and must be supplemented by equation (2). This latter relation has been used widely in the analysis of mineral parageneses

It is of interest that I. V. Alexandrov makes no attempt to prove the general error or the basic uselessness of the equation defining the number of the factors of state by any concrete example. He merely

insists that extensive parameters were neglected by Gibbs in his derivation of the Phase Rule as well as in some other cases. This is entirely correct, but is by no means a reason for the assumption of an error or of a futility of a wider utilization of the extensive thermodynamic parameters of state.

In the papers by V. A. Nikolaev [6] and A. V. Storonkin [7], dealing largely with a critique of my papers [3, 4], there is nevertheless an acceptance of the correctness of my derivation of equation (2). V. A. Nikolaev proposes incidentally to call the " $k + 2$ ", the number of factors of state, by the name of the "full variancy" of the system. I consider this an unfortunate term, for "variancy" of a system means, by the common usage, the number of degrees of freedoms, in accordance with the Phase Rule (for example, "monovariant", "divariant", "non-variant" systems). By the common rules of logic, "the full variancy" would sound like some special type of variancy and not like something fundamentally different. One has to speak, on many occasions, about the "conditional variancy" (V. A. Anosov), i.e. about variancy when some of the intensive factors of state are remaining constant (temperature, pressure). The "conditional variancy" is a natural opposite of the "full variancy" derived from the Phase Rule. For this reason, the expression "full variancy" as a substitute for the previously suggested "number of factors of state" or "number of independent parameters" appears to be incorrect.

I wish to commend the thoughtful attitude of I. V. Alexandrov in regard to his criticism of my papers, an attitude which provides a happy contrast with that of some of my earlier critics.

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CHRONICLE

The Seventh Session of the Committee on Determination of the Absolute Age of Geologic Formations

(VII Division of Geologic-Geographic Sciences, Academy of Sciences of the USSR, 8-12 May, 1958, Moscow)

The Seventh Ordinary Session of the Committee on Determination of the Absolute Age of Geologic Formations met May 8 to 12, 1958, at the Division of Geologic-Geographic Sciences of the Academy of Sciences of the USSR.

The Session heard and discussed more than 60 reports by scientists from Moscow, Leningrad, Kiev, Sverdlovsk, Makhach-Kaly, and other cities of the USSR on geochronology of different regions, together with a number of communications on methods.

D. I. Shcherbakov, Member of the Academy, in his opening speech, emphasized the necessity of a broader participation in determinations of the absolute age by the Institutes of Geology.

A. A. Polkanov presented a broad generalization of the data on Precambrian geochronology of the Baltic Shield, as indicated by the radiometric methods of determination.

N. P. Semenenko showed in his report that the Precambrian history of the planet, as a whole, may be divided into 4 megacycles, on the basis of the available data on the absolute age, namely:

1. 3200 to 2700 million years;
2. 2600 to 1900 million years;
3. 1800 to 1200 million years;
4. 1100 to 500 million years.

The post-Cambrian megacycle of 400 to 300 million years directly follows Megacycle 4, the Precambrian.

There were several reports on regional geochronology: Ukraine (L. V. Komlev et al.), Ural (L. P. Ovchinnikov), the report by A. P. Vinogradov's group on Eastern Germany, and others.

There was a high degree of interest in the paper by Iordanov, a Bulgarian scientist, dealing with a problem of the absolute age of a plutonic body in Bulgaria. This report was remarkable in the thoroughness of its investigations and in the finished form of its presentation. Great interest was shown also in the report by A. Ya. Krylov on applications of the argon method to clastic sedimentary rocks, in the course of which the author demonstrated the very good conservation of the radiogenic argon during the formation of sedimentary rocks.

We should note that the Seventh Session was definitely a turning point with respect to the attitude of geologists toward the methods of determination of the absolute age of geologic formations.

Not only was there a development of mutual understanding between radiologists and geologists but also a full recognition by geologists of the methods of absolute geochronology as working tools of geology, like chemical analyses. There was a strengthening of the regional laboratories whose independent results are now reliable.

The argon method, formerly in its development and testing stages, in regard to the range of its applicability, has now found its place among the classical methods of geochronology.

Among the reports on methods, we should emphasize the importance of E. K. Gerling's communication on the new K-capture constant for K^{40} which is unlike the formerly accepted one (the use of this new constant, in the argon method, yields higher results for the absolute age).

E. K. Gerling reminded the committee that the formerly accepted constant for the transformation of K^{40} was obtained on the basis of the Committee's endorsement of 1800 million years as the datum for the age of the Belomere rocks; this datum was apparently too low. In this connection, Academician A. P. Vinogradov proposed to discontinue the practice of the Committee to endorse the absolute age figures, since the previously endorsed figures are already in need of revision, in many instances, because of the refinements in the values of certain constants and of several unforeseen circumstances. It should be necessary, in all publications on the subject, to make detailed reports on conditions of the experiments and on the values of constants used in the calculations at the same time, so as to make it possible in the future to re-calculate the age findings with the aid of newer data.

The problem of conservation of argon in minerals used in determinations of age was stated and discussed in several reports. A method for isolation of the best-preserved fraction of argon and potassium, so as to assure reliability of the age data, was suggested in a communication by members of the Dagestan Branch of the Academy of Sciences of the USSR.

The report by N. I. Plevaya on application of the K/Ca method for determination of absolute age has met with considerable interest. This is the first report on this subject within the USSR.

As a summary, the Session admits that a substantial body of reliable measurements of absolute age has been accumulated to date, sufficient for a beginning of a construction of the Soviet geochronologic scale.

The construction of the geochronologic scale was assigned to a committee appointed for the purpose, with the participation of the leading workers in the field of geochronology.

V. I. Baranov, K. G. Knorre

The Second All-Union Conference on Petrography

The Second All-Union Conference on Petrography took place in the City of Tashkent, May 19-23, 1958, with the participation of more than 600 specialists from all over the Soviet Union as well as of guests from abroad. More than 20 professional papers were presented at the general sessions.

P. Ya. Antropov, Minister of Geology and Conservation, the USSR, gave two addresses at the general sessions. He spoke on the state of exploration of the territory of the USSR, the general state of geologic science, and on the problems on the agenda of the geologists, both fundamental and practical.

V. A. Nikolaev dedicated his report to a discussion of systems with unequal phase-pressures, in reference to certain processes involved in the endogenic formation of minerals.

D. S. Korzhinskii, in his paper "Acidity-Alkalinity as the Principal Factor in Magmatic and Post-Magmatic Processes", came to the conclusion that the "acid-alkaline hydrothermal differentiation" is the most important factor in the formation of post-magmatic mineral deposits, that the acid-base interactions of the constituents play a major part in the magmas themselves and not only in the magmatic aqueous solutions, and that acidified (aplitic) and alkalinized (lamprophyric) magmas indeed do exist. Diamagmatic solutions and abyssal magmas are primarily alkaline.

Yu. A. Kuznetsov proposed a classification of magmatic formations based on the principal types of tectonic structures and of the characteristics of the associated magmatism. His classification takes into account the petrographic features of the formations and their specific associations with certain definite types of geologic structures.

N. P. Semenenko reported on a genetic classification of metamorphic processes and rocks based on a differentiation of rocks into isochemical and isophysical series, depending on their chemical composition and on the extent of their metamorphism respectively. The metamorphic types are the distinctive foci, the stages in the discontinuous-interrelated metasomatic evolution of rocks.

V. P. Petrov called attention to the necessity of adoption of modern methods in petrographic research.

N. I. Khitarov, proceeding from experimental findings and from the analysis of certain features of volcanic eruptions, spoke to the effect that the bulk of water produced concurrently with eruptions of basaltic magma must be tied to the erupting magma itself and that it is feasible to regard basaltic magma as the least altered primary magmatic substratum. He discussed also the general course of "mainline" formation of rocks, as a process of successive transformations of the primary magma, chiefly in terms of variations in the H_2 - H_2O - O_2 system during the crystallization, with special attention to water as the main regulator of the process.

V. S. Kopteva-Dvornikova and co-authors gave summaries of the research by the staffs of the IGEM, GEOKhI of the Academy of Sciences of the USSR, and of the MGU, dealing with granitoids in different regions of the USSR. There was a discussion of granitic formations at shallow depths, of the admixture elements in their rocks, and of criteria for genetic relationships between intrusions and ores. The authors distinguish three categories of indications of a genetic relationship between mineralization and magmatic rocks:

- (a) Geochemical (including isotopic) affinities between intrusive rocks as such and the associated post-magmatic formations.
- (b) Geochemical affinities between post-magmatic formations and different stages of the vein rocks.
- (c) Geochemical affinity or identity of admixture elements in non-ferrous and in accessory minerals of vein rocks and in the corresponding minerals of post-magmatic origin.

Yu. I. Polovinkina's report deals with geologic relationships in the developments of magmatism within the territory of the USSR.

G. S. Dzotsenidze's communication drew attention to the role of effusive volcanism in the formation of mineral deposits.

The report by Sh. A. Azizbekov and co-workers was a characterization of magmatism and metallogeny in Azerbaijan, on the basis of geologic-structural aspects of the country.

A genetic relationship of mineralization to magmatism, with the Yali Caucasus as the example, was brought forth in the report by G. Magkian and S. S. Mkrtchyan.

Kh. M. Abdullaev reported on magmatism and the associated metallogenic processes in Central Asia, with an adumbration of the regional features of this area, as a typical province of acid intrusive rocks. The speaker, while discussing the stages of the development of magmatism and their place in the geologic history of different areas, made certain generalizations, such as the long duration of the pre-batholithic magmatic stage accompanied only by weak expressions of magmatic and ore-forming processes, the role of cyclic superimposed magmatic complexes and ore-forming processes, the development of Hartz magmatism, the hypabyssal character of intrusives, etc. There was a discussion of the evolution of metallogenic provinces in time and of a relationship between indications of ores to certain intrusions of a definite composition as well as of metallogenic characteristics of Central Asia and of problems involved in further studies.

E. D. Karpova, in her report, "Intrusive and Ore Complexes in Tectonic Zones of Southern Tyan-Shan," spoke of distinctions in the development of intrusive magmatism and metallogeny in different tectonic zones and of provincial characteristics of these zones and of the region as a whole.

D. N. Elyutin and co-authors threw some light on the formation of intrusive complexes against the background of the geologic history and evolution of some individual structural constituents of the N. Tyan-Shan

Zone. Characteristics of magmatism and metallogeny in Tadzhikistan were reported upon by R. B. Baratov.

The concluding session heard the reports by A. A. Polkanov and E. K. Gerling on the potassium-argon method of determination of absolute age and on the age of the Precambrian in the eastern part of the Baltic Shield, and the report by G. D. Afanasev, including data on the state of research in the absolute age of rocks and their geologic implications.

Also, there were communications by S. Dimitrov (Bulgaria) on "Magmatism and Ore Deposits of Bulgaria," Kautsch (German Dem. Rep.), on "Genetic Characteristics of Mansfeld Shales," M. Savul (Rumania), on "Applications of the Method of Liquid Inclusions to Petrogenic Problems," and K. Smulikovskii, on "Genetic Classification of Granitoids."

More than 70 reports were presented at the four sections dealing with problems of geology and metallogeny of Paleozoic and Mesozoic complexes, problems in alkali rocks, hyperbasites, and dike formations in geochemistry and physical chemistry of magmatic and metamorphic complexes and the methods of their studies. Considering the immense bulk of materials presented at the Conference, it is difficult to include many of the highly important and interesting data, both local and general, in a brief note. The interested readers should consult the recently published special edition: "Materials in Reference to the Second All-Union Conference on Petrography."

After the end of the Conference, there were two excursions for the delegates: to the Tashkent Area and Western Uzbekistan (longer than 1000 km) and to Kirgiziya. Many petrologically and metallogenically interesting objects and deposits were shown to the participants. Within the available time at the mines, preliminary brief lectures were given accompanied by demonstrations of the basic diagrams and rock specimens in addition to inspections in the field.

One must comment also on some weaknesses of the Conference: overloading of the agenda and the limited opportunities for a discussion of different topics. It should be rational in the future to present two or three topics, at most, for discussion by the geologic community, and to have these topics introduced by principal speakers accompanied by two or three associate speakers, as critics of the main report, in order to orient the general discussion of a given topic. The reports and the associate reports should be printed by the Program Committee one or two months before the Conference, by way of preparation for the general discussion at the Conference. The bulk of time should be allotted to the discussion, preferably with the inclusion of pertinent supplementary data. Statements made in the discussion are to be formalized in print after the Conference.

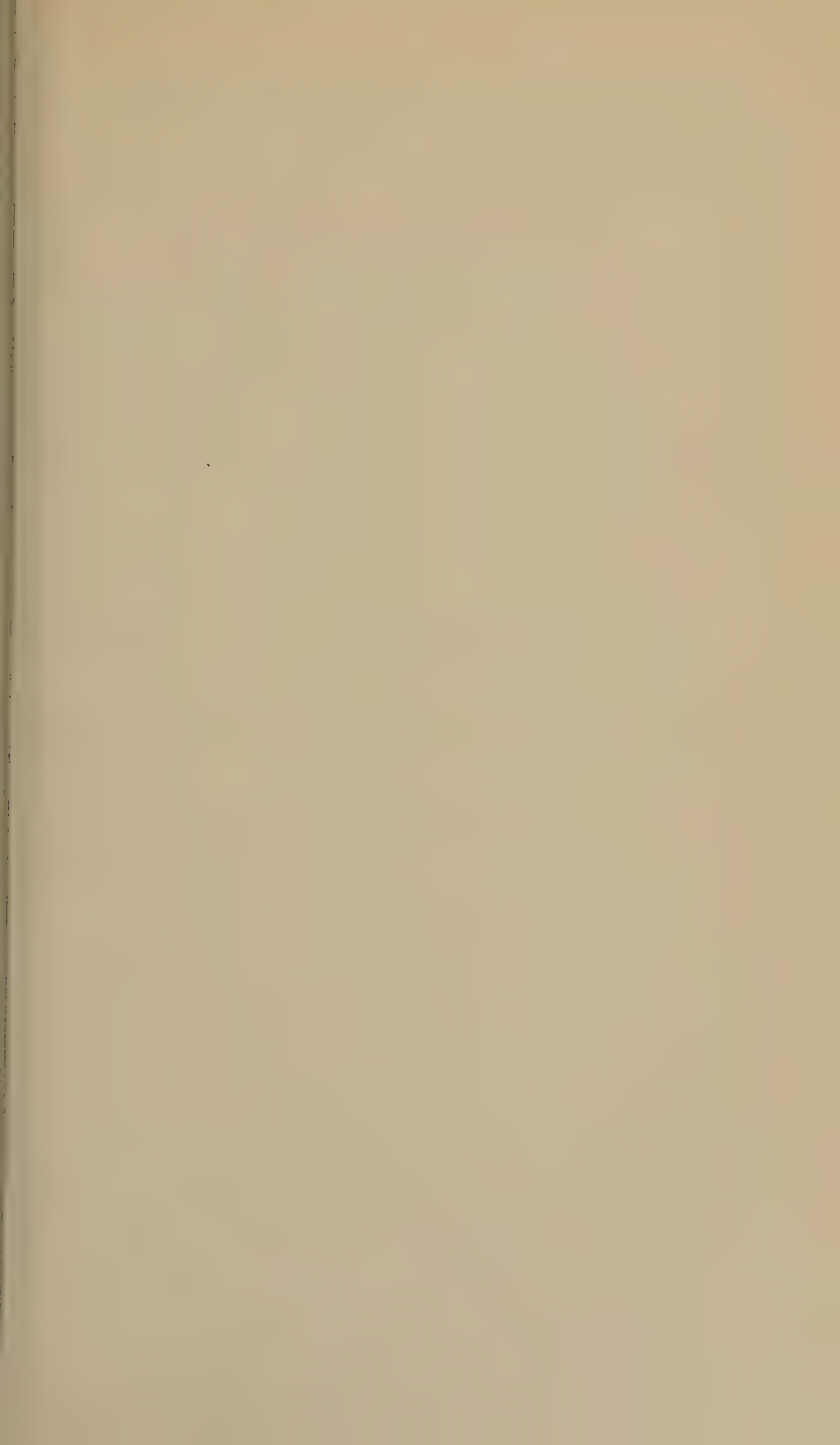
Despite the shortcomings here noted, the Second Conference on Petrography was a major event in the geologic life of the Union. The Conference served to summarize the work done since the First Conference, to pose a number of new problems, and to facilitate broad

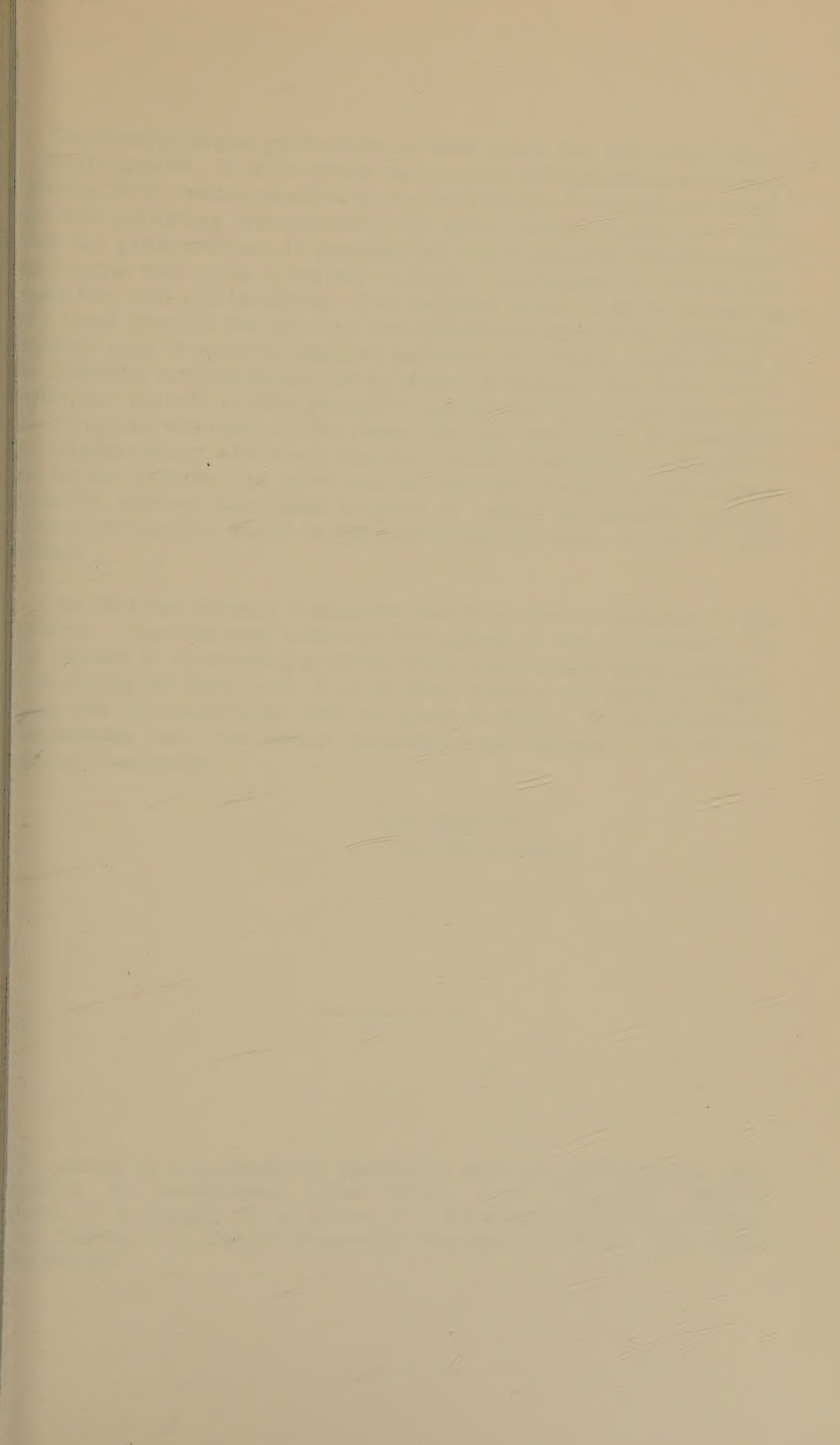
exchanges of views and development of professional contacts within the large circles of specialists from different parts of the Union, not only at the sessions but also in the lobbies and during the excursions.

It is not possible to omit commending the immense and the well done work of the Program Committee particularly by the comrades from Uzbekistan, as well as from Kirgiziya and Tadzhikistan, who gave much of their energy to the preparation and the conduct of the Conference which was acknowledged by statements of appreciation by many participants of the Conference.

The Third Conference on Petrography is planned to convene in Novosibirsk.

N. I. Knitarov





Geokhimiya began publication in 1956 under the able editorship of A. P. Vinogradov. It is the Soviet counterpart of *Geochimica et Cosmochimica Acta*, having practically identical fields of interest and coverage and publishing approximately the same number of pages per year. With the great increase in geochemical research in the U.S.S.R., there have come into being a variety of highly specialized journals in geochemistry and related fields. It is probably better to begin translating this more general journal first and follow with some of the more specialized ones if interest appears to justify this course of action and if the financial arrangements can be made. It is hoped that there will be sufficient interest in this journal to justify translation and publication (as complete volumes) of the issues for 1957 and 1956. If individuals and organizations who would purchase such translations will write to one of the Editors, the work will be undertaken when enough expressions of interest have been received to justify the expense involved. Prices presumably would be approximately the same as for the 1958 issues.

The National Science Foundation has been most cooperative in this venture. They not only indicated willingness to back it financially but also helped in calculating probable costs and possible subscription income during the first year. It is on these figures, and those for advertising and administration, that the grant is based. It is a pleasure to acknowledge here the advice, assistance and support of the National Science Foundation.

Earl Ingerson
Translation Editor

In matters of subscription for *Geokhimiya* refer to: Moskva K-104, Pushkinskaya, 23, Akademkniga. Chief Editor: A. P. Vinogradov. Editorial Council: V. I. Baranov, K. A. Vlasov, V. I. Gerasimovskii, D. S. Korzhinskii, A. A. Saukov, N. I. Khitrov (Responsible Secretary), V. V. Scherbina (Deputy Chief Editor).

Geochemical News is an informal bi-monthly newsletter published by the Geochemical Society and sent without charge to all of its members. It contains news of the activities of the Society, such as summaries of Council Meetings, reports of committees and plans for the future. It also includes announcements of forthcoming meetings and symposia of interest to geochemists, personalia, announcements or short reviews of books of geochemical interest, information on translations and translation services, letters and short notes by members, etc.

During 1959 the *Geochemical News* will contain a series of articles on research in geochemistry in laboratories in the United States, not only those associated with universities but industrial laboratories as well.

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New chemical data and interpretations involving chemical principles are emphasized. For example, papers in chemical mineralogy, petrology, oceanography and volcanology are acceptable, as are those in the chemistry of meteorites, whereas it would be suggested that those in descriptive mineralogy and volcanology, petrography, physical and biological oceanography and physical meteorites, be sent to other journals specializing in these subjects.

Thus, the subject coverage is closely similar to that of *Geokhimiya*. Also, the number of pages published per year is of the same order of magnitude. Subscription prices are as follows:

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